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THE PLASTICITY OF CLAYS.[1]

BY FRANK F. GROUT.

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THIS paper contains a method for measuring plasticity, numerically; the results of a series of experiments on the causes of plasticity followed by some observations on the condition of material in a plastic clay; and the conclusions reached. The work has been conducted in connection with the laboratory work of the West Virginia Geological Survey, in preparation of their Volume III, and it is a pleasure here to acknowledge the kindness which has made the investigation possible, as well as the valuable suggestions received from Dr. G. P. Grimsley, Assistant State Geologist, and other members of the Survey, and Dr. J. L. Sheldon of the Experiment Station.

The experimental data on the subject are meagre, and subject to criticism in the matter of the determination of plasticity. As stated by A. S. Cushman:[2] "There is unfortunately no better test for plasticity than the simple feel of the clay mixture." This injures all results thus far recorded, from the undeniable fact that one is likely to see or feel what he expects and hopes for. In view of the disagreement prevailing among clay workers, not only in the determination, but also in the definition of plasticity, these were the first points to be settled.

Definition: *Plasticity is the property developed in a clay by*

[1] Published by permission of Dr. I. C. White, director of W. Va. Geol. Survey.

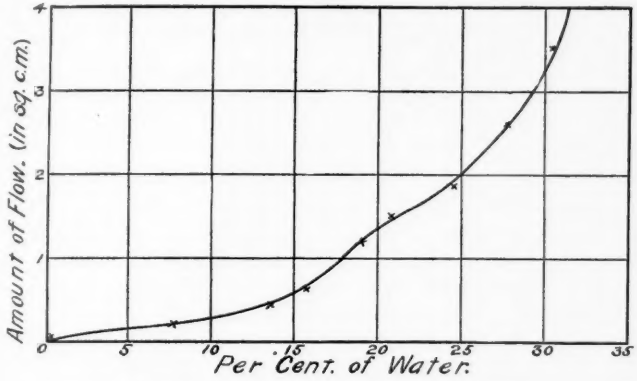
[2] *Trans. Am. Ceramic Soc.*, 6.

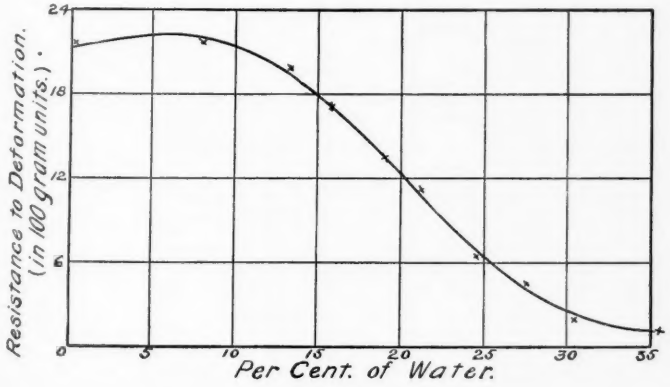
water, by virtue of which it can be molded, without crumbling, into forms which remain stiff and unchanged after the removal of the molding force. It is thus a double property, involving *strength* and *amount of deformation possible before crumbling.* The methods of determination heretofore suggested, have invariably neglected the second of these properties, and in some cases based the determination on some assumed relation between plasticity and other quite distinct properties. The use of tensile strength or cementing power of dried clay is an instance of the latter mistake. Its inaccuracy is shown by any extensive series of tests.[1] As examples of methods, which neglect the amount of possible deformation before crumbling, we have Bischof's method of forcing the moist clay through a die and measuring the distance it would project,—Dr. Ladd's measurement of the tensile strength of wet clay and Langenbeck's use of the Vicat needle.

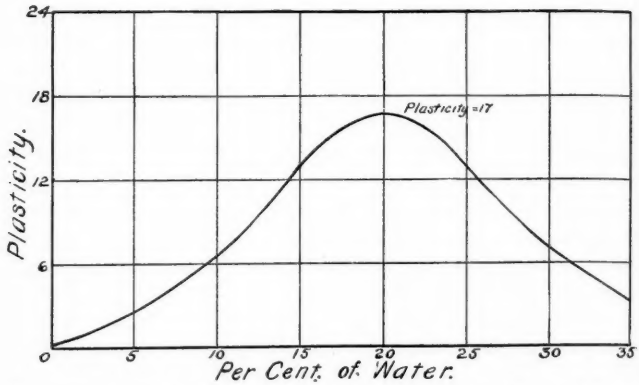
Experimentally, I have tried the simplest possible methods for each of these factors. Tests of compression and penetration were selected as more practical than tensile tests; the handling of unburned clay wares subjects them more often to compression than to tension. Various clays were ground to 40-mesh, tempered, and molded or cut into a variety of shapes. These were compressed and the effects noted. Cylinders were found to give the most uniform results and were easily produced of uniform texture, by tempering one hour, carefully mixing, forcing the mass into a thin walled metal cylinder 2 cm. in diameter, forcing out with a plunger, and cutting into 5 cm. lengths. To obtain the two factors, I recorded first, the weight necessary to compress the upright cylinder 1 cm., and second, the increase in area of the head of the cylinder when the cylinder was compressed to the point of fracture. This area was calculated from the amount of vertical compression, although, of course, the cylinder walls did not remain vertical as implied in the calculation. The fracture occurred as a number of cracks at about 45° to the direction of pressure. The appearance of the compressed cylinder is well shown in Fig. 8, Plate II, U. S. Geol. Survey, Bull. 241, "On Schistosity and Slaty Cleavage," by G. F. Becker. As the method was so simple, a number of readings were taken and the average values were used. It was found that the readings for strength (the weight required to compress the cylinder) varied much more than was

[1] G. E. Ladd: *Georgia Geol. Survey*, Bull. 6-A, p. 32; H. Ries: *Maryland Geol. Survey*, 4, 252 and 260.

desired, and this part of the determination was abandoned in favor of the Vicat needle. As the moist clay exerts considerable friction on the sides of the needle I used a needle of 7 sq. cm. section, so that friction would represent a smaller part of the total reading. As finally selected, the method is as follows: Strength was measured by the weight (in 100 gram units) required to force the needle 3 cm. into a mass of clay 4 cm. deep in half a minute. The amount of possible flow was measured by the increase in area of the cylinder as described above. The product of the two was considered the measure of plasticity at that stage of wetness. But, as the clay dried out, each factor varied in a smooth curve, and the product rose to a well-defined







EXPLANATION OF FIGURES.—The curves for Amount of Flow and for Resistance to Deformation are plotted from experimental data. Then the plasticity of the clay at any certain per cent. of water is found by multiplying the two readings for that per cent. The curve drawn through all such products shows the maximum plasticity of the clay. In this case it is about 17.

maximum at a definite per cent. of water. It was easily possible to measure these values at intervals as the clay dried, and plot curves, and from them, the curve for the product (see diagrams).[1] It is possible, in application of this method, to measure about 16 clays in an eight-hour day. Results range from 1 to 30 for lean and plastic material, respectively.

The following hypotheses have been advanced as causes of plasticity:

(1) *Fineness.*—Proved to be insufficient.[2]

(2) *Shape of Grain.*—Thin plates. This seems to be quite extensively credited,[3] but accurate results are hard to obtain, when the plates are less than 0.001 mm. in diameter.

(3) *Colloids.*—These have been stated definitely[4] to be capable of improving plasticity, but vital objections can be raised, as will be shown later.

(4) Various other theories are easily shown to be inapplicable.

[1] A study of various curves for plasticity revealed the interesting fact that clays undoubtedly vary in the *quality* as well as in the *maximum amount* of their plasticity, some having a sharp maximum, others a broad rounded curve.

[2] Beyer and Williams: *Iowa Geol. Survey*, **16**, 91.

[3] H. Ries: *New Jersey Geol. Survey*, **6**, 82; E. R. Buckley: *Wis. Geol. Nat. Hist. Survey*, Bull. VI, p. 25; H. A. Wheeler: *Ann. Rep. Mo. Geol. Survey*, 1896, p. 106.

[4] A. S. Cushman: *Trans. Am. Ceramic Soc.*, **6**.

EXPERIMENTAL.

The following experiments give a general idea of our results:

(1) *Fineness.*—Shale No. 63 at 40-mesh had a plasticity of 14. At this time about 50 per cent. of it was fine enough to pass a 100-mesh sieve. A duplicate was ground to pass 100-mesh, when the plasticity was 18. Shale No. 64 rose from 3 to 7 by similar treatment. Shale No. 40 gave the reverse result, dropping from 18 to 16. This was unexpected but has been found true in other cases. The majority improve, some are unchanged, and a few are injured a trifle.

It has been shown[1] that addition of sand injures plasticity directly as the diameter of grains increases. Clay No. 16 had a plasticity of 17; mixed with an equal weight of sand at 40-mesh the figure was 7; with sand at 100-mesh, 9. Several shales were only slightly affected by 25 per cent. sand, while others were seriously injured. This was probably due to the presence of some sand in the original clay, so that a small addition brought the total sand to a high per cent. The grinding of minerals not considered plastic gave the following figures:

Quartz at 100-mesh.....	2—.
Calcite at 100-mesh.....	3+.
Muscovite at 100-mesh.....	4+.

These figures are in excess of those obtained by our regular method applied to some flint clays.

(2) *Shape of Grain.*—The above experiment with powdered minerals is full of meaning in this connection. Microscopic work revealed the presence of abundant plates in many clays, but no definite results can be stated.

(3) *Colloids.*—Under this head we may discuss the effects of weathering (though the relation to colloids is doubtful), and the effects of adding colloids to clay; incidentally, also, the staining of colloids, their strength when dry, and power of hydration.

All clays, tested thus far, improve in plasticity by a few days alternate wetting and drying. Weathered river clays show very little change compared with shales. The extreme case was shale No. 64, which rose from 2.6 to 14 in two weeks. Air-drying did not destroy the improvement. The shales ground to 40-mesh weathered to approximately the same figure as the duplicates at 100-mesh. This suggested that the action might be largely mechanical. The

[1] Beyer and Williams: *Iowa Geol. Survey*, **16**, 86.

amounts of clay (below 0.005 mm.) in shale No. 63 were determined before and after weathering. The per cent. rose from 7.7 to 17.8 by one wetting and drying. Shale No. 63 was also used to test the action of bacteria. One of three samples of a clay was sterlized with chloroform in a bottle plugged with cotton. The chloroform was removed by thorough evaporation under diminished pressure. Sterile water was used in weathering and great care was taken to prevent any addition of bacteria. The second sample was weathered with city water (Monongahela River), and dried in open air. The third was kept dry. In a week they were tested.

Sterile weathered shale, plasticity.....	18
Ordinary weathered shale, plasticity ...	18
Unweathered shale, plasticity.....	14

It is certain, however, that bacteria can live in clay, and probably do add protoplasm to it; hence, organic colloids, which may increase plasticity in some cases. So much emphasis has been placed on weathering, in the discussion of colloids, that further light was sought, in the determination of combined water before and after weathering. After two weeks' weathering and large increase of plasticity, three samples were air-dried for twenty-four hours. Hygroscopic moisture varied from the original, some increasing, some decreasing. But when calculated to 100 per cent. without this free water, the combined water checked very closely with the original unweathered clay (0.02 per cent.). The amount of combined water in a clay does not change with rise of plasticity. An increase was noted in the soluble salts. Possibly the sulphides were oxidized, or the mechanical action exposed more surface to the solvent.

Two experiments will illustrate our results in adding colloids to clay. Two distinct types of substances were used, colloidal solutions and gelatinous precipitates. A very dilute solution of the agar-agar of bacteriologists was used instead of water in tempering two clays of plasticity equal to 7 and 11. The figures were increased to 11 and 15 respectively, by as small an addition of agar as 0.08 per cent. of the weight of the clay. The addition of 0.2 per cent. caused a further increase, but not in proportion to the amount added. Now one of the great objections to the colloid theory[1] is "the very small and inconsiderable proportion

[1] Beyer and Williams: *Iowa Geol. Survey*, **16**, 90.

of ingredients which are capable of assuming the colloid state by the action of water alone." It will be noticed that 0.2 per cent. is an inconsiderable amount which produces an effect well worth considering. Further, agar has a gelatinizing effect ten times as strong as gelatine, another colloid. It is conceivable that some substance may be even more active than agar, so that a few hundredths of a per cent. may increase plasticity remarkably. After the agar was added, the samples were air-dried, gently crushed to 40-mesh, and the plasticity measured. It was as high as when agar was first added. Ten grams of the air-dried samples were heated with water and settled for a determination of the soluble salts. It was supposed that the presence of a colloid would be noted in that determination. *No jelly could be obtained.* To further test for the presence of a soluble colloid the whole sample was washed with hot water on a porcelain filter for two days. Its plasticity was unaffected. The same was true for a plastic clay (No. 16) which had not been treated with agar.

Alumina-cream was washed by decantation and used without drying, instead of tempering water. It required an amount (measured as Al_2O_3) equal to 3 per cent. of the weight of the clay to raise the lean clay (7) as much as 0.08 per cent. agar (11). The mass was then air-dried, powdered, and the plasticity measured. It had dropped to the original figure (7). Weathering a week increased it less than half a point. As plastic clays are not thus injured by air-drying it is evident that such colloids as alumina cream do not explain plasticity. Some colloid is required which will soften in water after air-drying, and these are extremely rare in the inorganic kingdom. The suggestion of some recent writers,[1] that a hydrated silicate of alumina could be precipitated so as to give the desired properties, has been carefully tried, but all resulted exactly as the alumina cream. Most of the silicate was prepared by mixing sodium silicate and alum solutions, both of which are supposed to occur in clays as decomposition products of other minerals. No precipitate was obtained which would appreciably soften after air-drying. The assumption that some unknown silicate of alumina possesses such a property is unjustified by the known properties of inorganic colloids.[2]

[1] A. S. Cushman: *Trans. Am. Ceramic Soc.*, **6.**

[2] A recent writer ascribes the viscosity of colloids to a physical heterogeneity of the solution. Many authorities find no distinct line between colloidal solutions, colloidal suspensions, and other suspensions. With this in mind it may be said, that the finest

The fact that colloids are stained by methylene-blue has recently been presented in the discussion of colloids.[1] I find that most clays contain from 1 per cent. to 5 per cent. of grains which will take a stain from methylene blue, gentian violet, eosin, or fuchsine. These might be classed as colloids or "pectoids," though their exact nature is undetermined. For, I find much organic matter will take such stains; freshly gelatinized silicic acid will stain easily; *air-dried silicic acid jelly will take the stain with equal readiness.* Now, air-dried silicic acid has an action *identical with angular quartz sand* in affecting plasticity of clay, injuring, instead of causing plasticity. Some clay grains which stained very little showed a border or spot of color, agreeing with the idea that the production of this form, capable of being stained, is due to some secondary action. But weathering, with its remarkable increase in plasticity does not materially increase the number of grains taking the stain, nor the depth of color. The observation of "minute spherical particles, which may be of colloidal character,"[2] thus loses some importance. The fact that they are amorphous does not necessitate softening in water. In this connection, a recent writer[3] has found that high magnification reveals crystalline structure in the "globules" of Zettlitz kaolin, which have long been considered amorphous.

The value of strength tests, in discussing colloids, is indirect. Plastic clays are often strong. Colloids added to a powder, often increase its strength. Hence, it is argued, colloids are in clay. But the conclusion is not inevitable. Colloids, like air-dried silicic acid, *decrease* strength, and in studying the substances which *increase* it, we find that not only colloids like agar but crystalloids like gypsum and alum, are quite active.

The absorption of hygroscopic water is another indirect argument. Clays absorb water. Colloids absorb water. Hence, it is said, clay contains a colloid. But it may be a colloid like dried silicic acid, so that nothing is indicated in connection with plasticity. The colloid structure is admittedly destroyed by ignition, but we have found some thoroughly ignited clays which

clay particles *do* remain suspended indefinitely; they *can* be coagulated like colloids by heat or the addition of salts; possibly they are active in increasing viscosity, and thereby, also plasticity. But this is not the meaning of the colloid theory as it is usually stated.

[1] A. S. Cushman: U. S. Dept. Agr., Bur. of Chem., Bull. 92.

[2] H. Ries: *New Jersey Geol. Survey*, **6**, 83.

[3] S. Kasai: *Z. Kryst. Min.*, 1899, p. 653.

absorbed water in amounts quite comparable with unignited clay, after standing in moist air.

CONDITION OF A PLASTIC CLAY.

After a little kneading, each grain in a mass of clay is wet on all sides by a film of water. Of course, if the grains are angular and the water is not abundant, or if the pressure is considerable, the adjacent grains may penetrate the film and come in direct contact. But through some force—call it capillarity, or surface tension, or some other[1]—the water spreads in films around the grains. The cohesion of water, the adhesion of clay grains and water, and the cohesion of clay through the water films, unite to make the moist clay hang together. At the same time the water films act as lubricants. This combined cohesion and lubrication forms the ultimate basis of plasticity. A simple illustration is the action of two glass plates with water film between. When dry, friction is great and cohesion small, both in case of the ground clay and the glass plates. As water is added friction decreases till no greater than that of the liquid. Cohesion meanwhile becomes large, just as enough water is added to wet the surfaces, and then steadily decreases when excess of water is added.

Plasticity, as defined above, will depend on two factors; first, the *distance* the clay particles can move on each other without losing coherence; and second, the *amount* of that coherence, or the resistance to movement. Under the first factor we find that the distance will vary with (*a*) the shape and size of grains and with (*b*) the distance through the film that they will attract each other. Under the second factor we find the resistance to deformation will depend on (*c*) the friction in the film and (*d*) the friction of the grains on each other, as they become irregular and penetrate the film.

(*a*) It is evident that two plates 2x2x$\frac{1}{4}$ inches will glide farther without losing coherence than two blocks 1x1x1 inch, though the bulk is the same. Again, angular grains may cohere, but relatively small movement will cause such a separation, due to the rough surfaces, that coherence becomes inappreciable. Again, two blocks 1x1x1 inch could be extended into a coherent mass of much greater length if the blocks were subdivided. Fineness also increases the surface exposed, requires more water, and thus improves lubrication.

[1] G. E. Ladd: *Geol. Survey of Georgia*, Bull. 6-A, p. 31.

(*b*) The attraction of two clay grains may vary, with the nature of the grains. The greater the attraction the farther they can be separated without losing coherence. This will be discussed presently in detail.

(*c*) The film may produce more friction to gliding in several ways. It may become greater in area. The friction of two plates 2x2x¼ would be four times as great as two blocks 1x1x1. Again the film may become viscous. The action of colloids is probably at this point. Another way in which the films become viscous is the result of molecular attraction, which *binds* a film over the surface of the grain and renders it viscous.[1] The thinnest films are most viscous, and the films attracted most strongly by the grain are most viscous. The friction between this film and the solid grain of clay, is said to be infinite, compared with water outside of the film.[2] But when forced to move the resistance would depend on the strength of the attraction of clay and liquid.

(*d*) It is evident that wet rough sandstone will exert more friction than wet polished glass.

Twice in the above summary of the possible variations in a clay I have referred to molecular attraction. This is yet to be justified. The extremely small range of its influence seems to render it insignificant. Quincke finds that glass attracts water in this way for 0.00005 mm. Other men and methods give results of the same order of magnitude, this figure being the one quoted by the text-books. Now a simple calculation, based on the mechanical analyses of clays, will show[3] that the amount of water needed, to place a film 0.00005 mm. thick around each grain is

[1] Dr. Ladd (*Ga. Geol. Surv.*, Bull. 6-A) mentions that the "mutual attraction" of clay and water is so great that it gives a certain "rigidity" to the water, thus giving strength to a clay when it is so wet, one would expect it to be quite fluid. But he gives no data to show that this cause is sufficient to produce the results mentioned. In fact, he refers mainly to capillarity (p. 21), whereas, the rigidity is to be found only in the sub-capillary films. He further attributes the "pull" to *chemical composition* (p. 31), which we will consider later. Beyer (*Iowa Geol. Surv.*, **16**, 97) also speaks of the physical attraction of particles for the surrounding one through a film of water, but he fails to note the effect on viscosity and the fact that attraction may differ, with different substances.

[2] Daniell, Alfred: "A Text-book of the Principles of Physics," 3rd Ed., Macmillan Co., p. 306.

[3] Our mechanical analyses frequently show a large per cent. of grains below 0.001 mm. in diameter, also from 0.001 to 0.005 mm. The average diameter of grains below 0.001 mm. is 0.0005 mm. If these are considered spherical and of specific gravity 2.5, it would require 25.5 per cent. by weight of water to place around each grain a film 0.00005 mm. thick. If the grains were considered plates one-fifth as thick as wide, instead of spheres, over 54 per cent. of water would be required. Then in an average "fine clay," 40 per cent. of water will produce only sub-capillary films. A similar calculation for the clay from 0.001 to 0.005 mm. in diameter shows that it would require 8 per cent. Thus many of our clays require 25 per cent. of water to produce these films.

often nearly equal to the amount added in tempering. So that in ordinary plastic clay, it is necessary to consider practically all the water as being under this influence. The change in viscosity or in thickness of the film, seems to be beyond the region of experiment. The quantity is too small to admit the determination of slight changes, but such are constantly assumed in physical problems. W. J. A. Bliss,[1] speaks of clay particles and the surrounding adherent liquid, as follows: "*The thickness of this shell depends on the intensity of the attraction between the solid and the liquid.*" J. E. Mills,[2] says, "*molecular attraction depends primarily on the chemical constitution of the molecule.*" This is the essential fact of our theory. Some hydrous silicate of alumina attracts and holds a thicker film of water in a viscous condition than most powders. Another factor besides the constitution of the solid is the quality of the liquid. Slight amounts of soluble salts in the water will change the attraction. W. J. A. Bliss, in the above-mentioned article, suggests this explanation for the coagulation of suspended clay particles and the reverse effect by other salts.

The molecular constitution on which this theory rests, is not to be confused with composition. Kaolin may or may not be plastic. Amorphous varieties have been appealed to in explaining the variation in kaolin, but this may not be necessary. Dr. F. W. Clarke suggests[3] seven possible formulae for crystallized kaolin; two being more probable than others. Our suggestion is that at least *two exist*. Similar changes are suggested[4] to account for changes in the physical properties of other silicates, *e. g.*, orthoclase

[1] *Phys. Rev.*, **2**, 373 (1894-5).

[2] *J. Phys. Chem.*, 1902, p. 209.

[3] In *U. S. Geol. Surv.*, Bull. 125, Dr. Clark recommends the formula $Al{<}^{OH}_{(SiO_4)Al}(SiO_4)K_3$. The kaolin, however, is a very stable compound, and, as he suggests, the group $-(SiO_4)H_3$ is doubtful. The stability also favors a more symmetrical arrangement. In quite an extensive series of tests in our laboratory no difference was found in the ease of extracting the atoms of any one element of the kaolin. Comey's "Dictionary of Solubilities" refers to Malaguti as authority for the extraction of one-fourth of the silica by potassium hydroxide. We could not confirm this. Sulphuric acid, bromine, chlorine and ammonium chloride, if used at a temperature and concentration to attack kaolin, will do so progressively and, in the end, completely. We therefore favor the formula $Si_2O_5.2Al(OH)_2$, credited to Groth. The diorthosilicate is also symmetrical, $Si_2O_7.K_4(AlO)_2$; but the group $Si_2O_7.H_4=$ should be open to the same objection as the group $-(SiO_4).H_3$ Several other complicated symmetrical formulas can be imagined, but the simplest, most symmetrical is the dimetasilicate of Groth's. The trisilicate offers the most evident opportunity for isomeric salts, but does not offer a symmetrical arrangement. This, of course, does not effect the evidence found in the relation of kaolin to other silicates, which led Dr. Clarke to recommend the first formula mentioned.

[4] Van Hise: *U. S. Geol. Survey*, Mon. XLVII, p. 202.

and microcline. In case of kaolin we may therefore imagine a change in physical properties, due to the chemical constitution of the molecule, but considerable experimental work has not suggested wherein the constitution varied, nor how one might hope to obtain the desired form.

SUMMARY.

(1) Sand injures plasticity little at first because the grains are suspended in a plastic mass. It is only when grains are abundant enough to come in contact with their neighbors, that the effect becomes serious, and then both strength and amount of possible flow are injured.

(2) Certain rare organic colloids increase the plasticity by rendering the water viscous.

(3) Fineness also tends to increase plasticity.

(4) Plane surfaces (plates) increase the amount of possible flow. They also give a chance for lubrication by thinner films, thus increasing the friction of film, and the strength of the whole mass. The action of plates is thus twofold; but fineness may be carried to such an extent as to break up plate-like grains into angular fragments. The beneficial effects of plates are also decreased by the fact that each is so closely surrounded by others in the mass.

(5) Molecular attraction is twofold in increasing plasticity. As the attraction increases, the coherence and strength of the mass increase, and the amount of possible deformation before crumbling also increases. Fineness increases this action by requiring more water. Colloids and crystalloids in solution may also increase the attraction. It is thus seen to be more active than any other single factor.

CONCLUSION.

Molecular attraction depending on the chemical constitution of molecules is the chief cause of the high degree of plasticity found in clays. But practical work in improving clays[1] may well follow the lines already started; first, the addition of such colloids

[1] The tendency for tensile strength to vary with plasticity is also easily explained in this way. Molecular attraction between two kaolin grains may be high. If the attraction for water is high, some water will be drawn between the grains and rendered viscous by the attraction; this makes plasticity high. But when the water dries out from such a mass, the kaolin grains still attract each other, and the chances are for greater strength than when wet, because the water has acted as a lubricant, allowing a readjustment of grains to fill the space left as the water moved out. The result is a high degree of consolidation

as tannin, etc., or such solutions as ammonia, alum, etc., which can be shown by experiment to produce the desired results; and second, weathering, with its mechanical action and its possible addition of colloids by bacteria.

W. VA. GEOLOGICAL SURVEY.
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LIQUID MIXTURES OF MINIMUM BOILING-POINT.

BY C. D. HOLLEY AND J. T. WEAVER.

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THREE YEARS ago one of us, C. D. Holley,[1] presented the results of an investigation of sixteen pairs of liquids of which amyl alcohol or its derivatives formed one constituent. Of these sixteen pairs, five gave mixtures having well-defined minimum boiling-points, two showed no relative elevation or depression of the boiling-point and the remaining nine presented no unusual phenomena. In this paper the writer reports the results obtained with a series of pairs of liquids with propyl and isobutyl derivatives as one of the constituents, together with some miscellaneous curves. The investigations made with carbon tetrachloride were carried out under the direction of the writer by J. T. Weaver in the North Dakota Agricultural College Laboratory.

The apparatus and methods of procedure were the same as described in the previous article, a Hite's apparatus provided with a thermometer reading to fifths being used. A weighed amount of the lower boiling constituent was introduced into the bulb and boiled for several minutes, the boiling-point and barometric pressure being noted. Weighed amounts of the other constituent were added and the successive boiling-points recorded until the liquids were present in nearly equal proportions. The process was then reversed beginning with the higher boiling constituent.

The liquids used were supposed to be chemically pure as purchased, but before being used were further purified by distillation, the first and last fourths being rejected. The bulb of the Hite apparatus was kept covered and the distillation carried on in subdued light, and it is believed that the bromides underwent very slight, if any, decomposition. From twenty-five to thirty readings were made with each pair of liquids, and as the minimum point was approached the successive portions of the added con-

[1] This Journal, **24**, 448 (1902).

stituent were diminished in quantity so that the ratio of the constituents which gave the minimum point was definitely obtained.

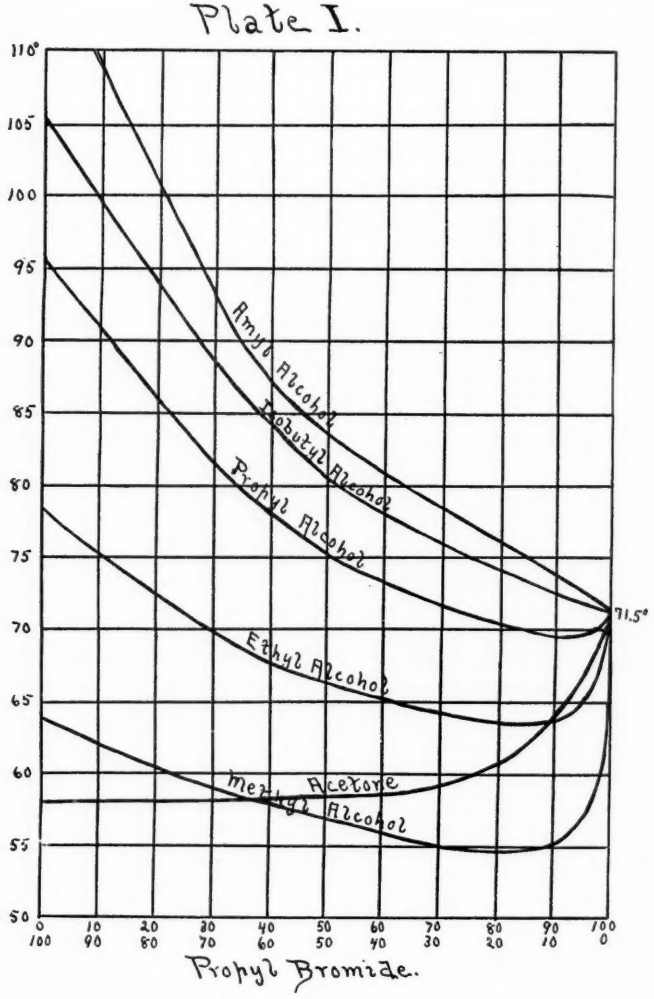
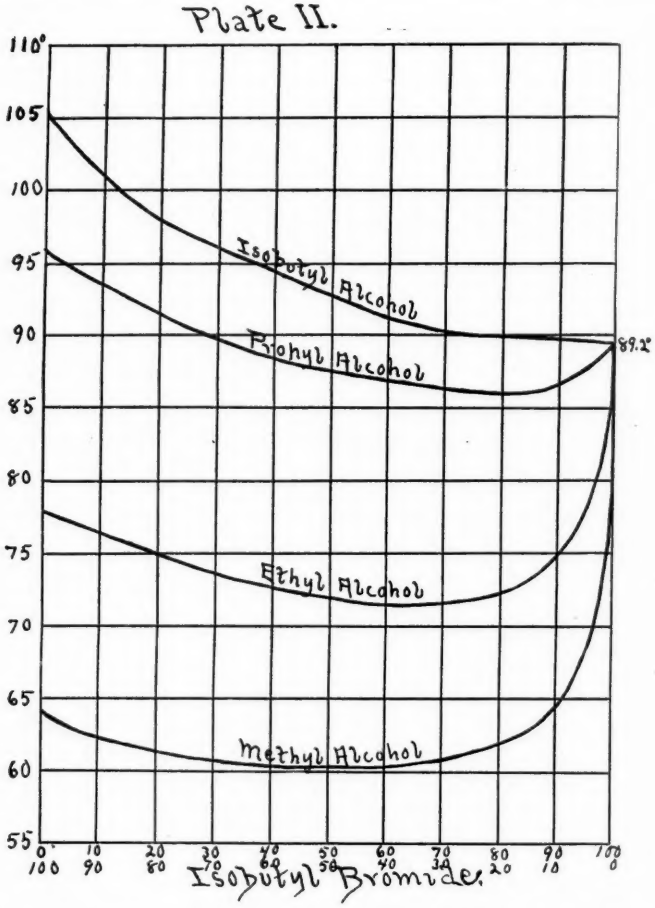


Plate I represents the boiling-point curves for propyl bromide with methyl, ethyl, propyl, isobutyl and amyl alcohols and also

with acetone. The addition of propyl bromide (71.5° C.) to amyl alcohol (129.3° C.) and isobutyl alcohol (105.5° C.) rapidly lowered their boiling-points but did not give a minimum point, though there was a tendency in that direction as indicated by the waviness of the two curves. Propyl alcohol (95.6° C.) gave a mixture having a minimum boiling-point of 69.75° C., in the ratio of 10 parts propyl alcohol to 90 parts propyl bromide, the minimum point being 1.75° below that of propyl bromide, the lower boiling constituent. Ethyl alcohol (78.4° C.) gave a rather interesting curve. It is obvious that the ratio of the constituents can be varied widely and yet give mixtures which have a boiling-point below that of the lower boiling constituent. The minimum point obtained was 63.6° C. or 7.9° below that of the propyl bromide, the ratio at that point being 16.24 parts ethyl alcohol to 83.76 parts propyl bromide. The curve obtained with methyl alcohol (64.0° C.) has the same general characteristics as the preceding ethyl alcohol curve, but much more intensified, the minimum point being 54.8° and the ratio 20.60 parts methyl alcohol to 79.40 parts propyl bromide. The minimum boiling-point obtained was 9.2° below that of the methyl alcohol, the lower boiling constituent. The effect of additions of propyl bromide to acetone was rather odd as it gave neither an appreciable depression nor elevation of the boiling-point until the mixture contained over 60 per cent. propyl bromide, then giving a curve which is characterized by its extreme flatness.

Plate II shows the boiling-point curves of isobutyl bromide (89.2° C.) with methyl, ethyl, propyl and isobutyl alcohols. As in the preceding series of curves isobutyl alcohol does not give a minimum point, though the range between the boiling-points of the isobutyl bromide and isobutyl alcohol is much less than the range between isobutyl alcohol and propyl bromide, the difference being 34° and 15.3° respectively. Isobutyl bromide and propyl alcohol gave a mixture having a minimum boiling-point of 86.1° in the proportions of 19.25 parts propyl alcohol to 80.75 parts isobutyl bromide, the minimum point being 3.1° below the boiling-point of the isobutyl bromide. Ethyl alcohol gave a mixture with a minimum boiling-point of 71.4° with a ratio of 41.0 parts ethyl alcohol and 59.0 parts isobutyl bromide. As in the preceding series of curves the one obtained with methyl alcohol resembles the ethyl alcohol curve closely, a minimum boiling-point

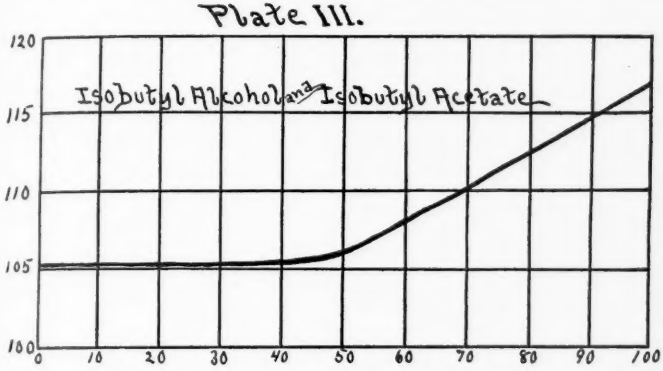
of 60° being obtained, but this point is not definitely located on the curve, as the mixture may contain anywhere from 41 to 56 per cent.



of isobutyl bromide without any resulting change in the boiling-point.

Plate III. Isobutyl alcohol (105.5° C.) and isobutyl acetate (116.3°) as indicatd by the curve did not give a mixture having a minimum boiling-point. The first six additions of isobutyl

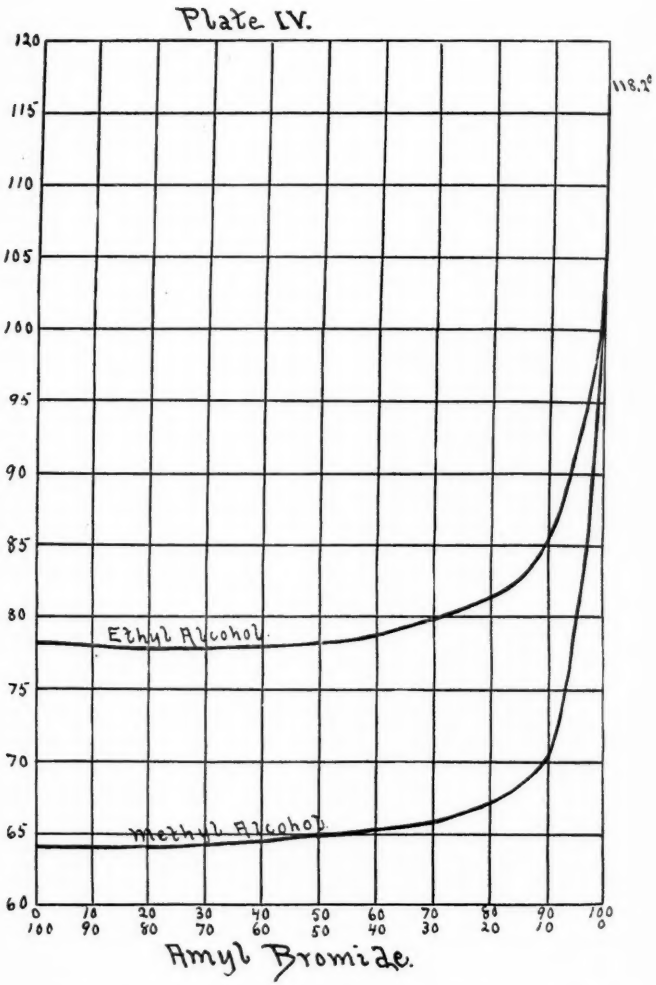
acetate did not lower or raise the boiling-point of the isobutyl alcohol. The mixture contained at this point 40 per cent. isobutyl acetate; further additions of acetate caused a gradual rise of the



boiling-point of the mixture, the remainder of the curve taking the form of a straight line connecting this point with the maximum.

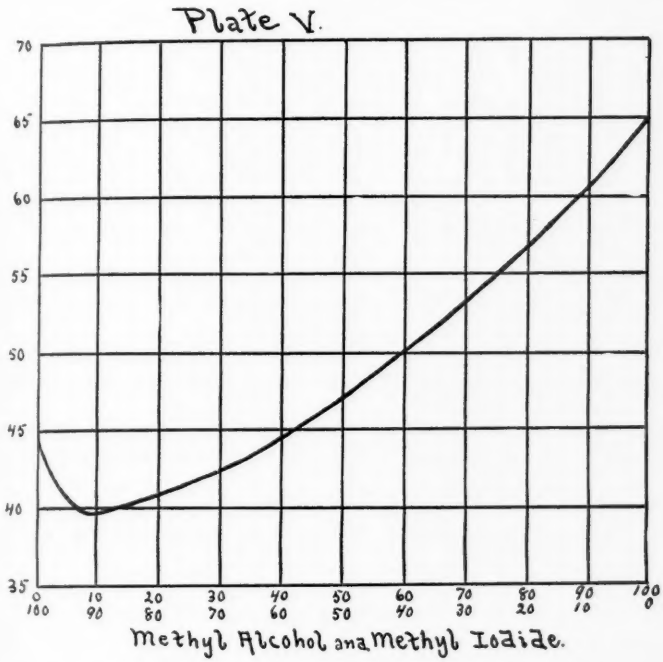
Plate IV represents the completion of the amyl bromide series begun in the writers' previous article. The three higher alcohols, propyl, isobutyl and amyl alcohols, gave mixtures having fairly well-defined minimum boiling-points, though there was the same tendency toward flatness that is exemplified to a marked degree in the two curves here shown; ethyl alcohol (78.3° C.) and amyl bromide (118.2° C.) gave a mixture having a minimum boiling-point of 77.3° C. in the ratio of 72.0 parts ethyl alcohol to 28.0 parts amyl bromide. The minimum point is not as clearly defined as with the higher alcohols. The additions of as much as 10 per cent. of amyl bromide caused no change in the boiling-point of the methyl alcohol (64.0° C.), further additions causing slight elevations of the boiling-point of the mixture. The effect of very small additions of either methyl or ethyl alcohol to pure amyl bromide is to be noticed, the boiling-point of the amyl bromide being lowered nearly (50° C.) by the addition of 5 per cent. of methyl alcohol.

Plate V. Methyl alcohol (64.8° C.) and methyl iodide (44.5° C.) gave a mixture having a minimum boiling-point of 39.6° C. in the ratio of 8 parts methyl alcohol to 92 parts methyl iodide. The



curve drops very abruptly to the minimum, which is very close to the methyl iodide side, then rises in a sweeping curve to the maximum.

Plate VI. Contrary to expectation butyric acid and bromoform gave a mixture having a minimum boiling-point. The

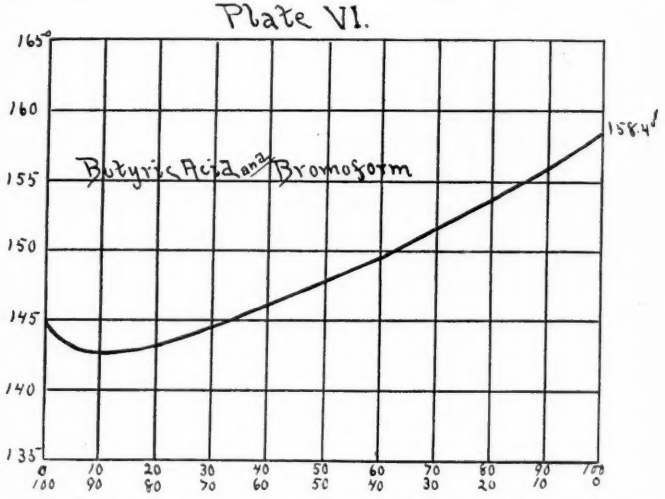


butyric acid used was obtained from Richards & Co., and though marked "C. P." was a very poor article. After several fractional distillations, a portion consisting of about 40 per cent. of the original amount was obtained which distilled between 158° C. and 159° C. The bromoform was obtained from the same company. After several distillations its boiling-point was much lower that it should have been. A portion was obtained finally which distilled uniformly at 145.5° C. A further quantity was procured from Merck & Co. but gave no better results.

The minimum boiling-point obtained was 142.6° C., the proportion being 87.5 parts bromoform and 12.5 parts butyric acid. The curve does not present any unusual characteristics.

Plate VII. Carbon tetrachloride with propyl alcohol, benzene and toluene. This plate shows the boiling-point curves obtained with mixtures of carbon tetrachloride (76.7° C.) with propyl alcohol (95.5° C.), benzene (79.6° C.), and toluene

(110.3° C.), respectively. Propyl alcohol gave a mixture having a minimum boiling-point of 72.6°, the ratio being 11.80 parts



propyl alcohol and 88.20 parts of carbon tetrachloride. The curve drops rapidly to the minimum point and then rises in nearly a straight line to the maximum. Carbon tetrachloride and benzene, which from the closeness of their respective boiling-points might be expected to yield a boiling-point curve with a well-defined minimum point, do not present any unusual phenomena at all, the curve being very nearly a straight line as is also the curve obtained with toluene and carbon tetrachloride.

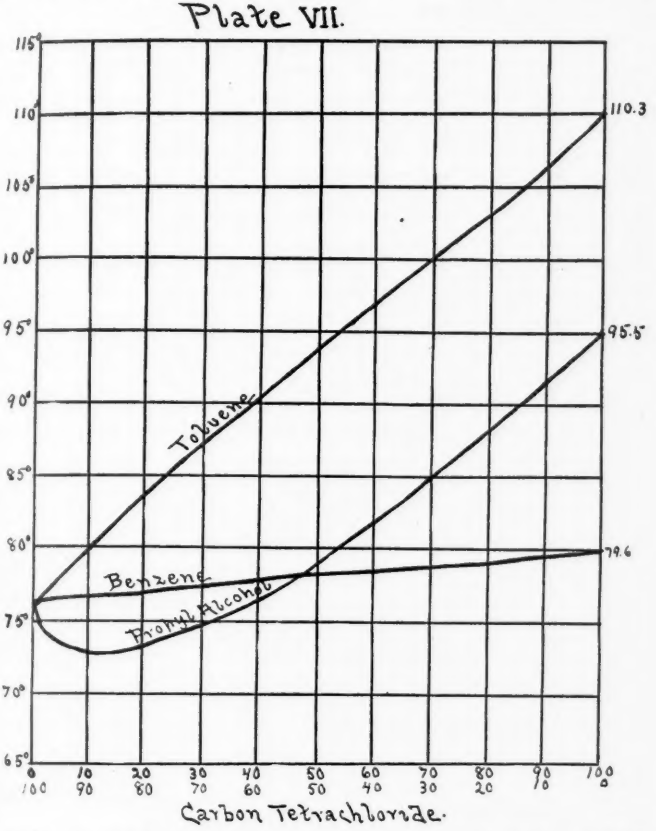
The following pairs of liquids were experimented with but no mixtures giving a minimum boiling-point were obtained:

Isobutyl alcohol (105.5° C.) and ethyl butyrate (120.6° C.).
Isobutyl alcohol (105.5° C.) and amyl acetate (137.5° C.).
Isobutyl iodide (120.4° C.) and bromoform (147.0° C.).
Isobutyl iodide (120.4° C.) and amyl acetate (137.5° C.).
Isobutyl iodide (120.4° C.) and ethylene bromide (129.8° C.).
Brombenzene (129.9° C.) and ethylene bromide (129.8° C.).
Bromoform (147.2° C.) and ethylene bromide (129.8° C.).

CONCLUSION.

Of the twenty-five pairs reported on in this investigation ten

gave mixtures having minimum boiling-points, three showed no relative elevation or depression of the boiling-point, and the remaining twelve pairs presented no unusual phenomena. As shown in the previous investigation, the chemical constitution



exercised a greater influence on the formation of mixtures with minimum boiling-points than the close proximity of the boiling-points of the constituents. One constituent remaining the same, mixtures with substances of similar chemical constitution yield similar boiling-point curves.

NORTH DAKOTA AGRICULTURAL COLLEGE.

A STRONG, STERILIZABLE DIALYZING MEMBRANE.

By Hibbert Winslow Hill.

Received June 23, 1905.

The use of dialyzing membranes in chemistry and physics has been long established. In the effort to apply dialysis to bacteriological problems, difficulties were found, principally due to the necessity for sterilization of all materials used, in order to prevent complications arising from the action of bacteria other than those under investigation. One material after another, physically adapted for dialysis, was rejected because it could not be sterilized satisfactorily. Collodion, dissolved in ether and alcohol, and by dexterous manipulation converted into test-tube-like sacs, received much attention from bacteriologists, since sterilization of such sacs is possible, and dialysis rapid. The technique, however, is very exacting; everything must be just right to secure results at all reliable; the collodion tissue is very fragile; and little satisfactory work is known to the writer as having been successfully done in dialyzing bacterial products by this method.

The method here to be described is extremely simple. While designed primarily for bacteriological purposes, it may be of interest to chemists and physicists also.

The resulting membrane is exceedingly strong; it can be handled, dry or wet, without injury; it may be repeatedly sterilized in boiling water, free steam or steam under pressure, and dialyzes well. It dialyzes less readily than does fresh collodion, which is, however, rather an advantage, for fresh collodion membranes, if not allowed to dry, dialyze so quickly as to suggest leakage, while if once dried, collodion membranes, in the writer's experience at least, become irremediably waterproof. The membrane here described can be set aside to dry, and, except that in this condition it is somewhat brittle, and by exceedingly rough handling may be injured, no evil result necessarily follows, the membrane becoming soft, pliable and permeable again immediately on immersion in water.

The chief advantages of this method are the multiplicity of sizes and shapes in which the membranes may be made, the strength of the membranes, their sterilizability and the simplicity of the technique, which, among other things, permits the testing of the integrity of the membranes at a stage where, if flaws are found, they can be eliminated before going further.

While not aware of anything similar already published, the writer has not been able to go into the literature of the subject sufficiently to satisfy himself that the method is strictly new.

Technique.—1. Make, from close-meshed, rigidly woven silk, square, circular, cylindrical, conical, bag-shaped or otherwise-shaped "frames" to act as the bases of the membrane desired. White taffeta silk, costing about one dollar a yard, is entirely satisfactory; also the silk used in the Edison mimeograph process, for taking the wax impression. The seams, if cylindrical, conical or other shapes of membrane in more than one plane are desired, should be flat and sewed double or treble, very firmly (best with a sewing-machine), the object being to leave no part of the seam less close or rigid than the mesh of the silk itself. Square or circular frames, and the mouths of bag-shaped frames, may be hemmed, making them practically untearable.

2. Dip this "frame" into a hot, filtered, 20 to 30 per cent. aqueous solution of gelatin standing on a water-bath at or near 100° C. Leave it in the hot gelatin long enough to thoroughly saturate the interstices of the silk strands as well as to fill the meshes, *i. e.*, about ten to fifteen minutes.

3. Raise the "frame," lifting it by safety-pins attached to its edges and allow it to drain freely. Safety-pins are used, because at this stage and later the membrane is extremely slippery. With the high percentages of gelatin prescribed, it is unlikely to drain too much (*i. e.*, until too thin a film remains) at ordinary room temperatures, but if any doubt is felt on this point, it is sufficient to reimmerse and quickly withdraw one or more times, until the operator is satisfied with the thickness and homogeneity of the film.

4. When the gelatin no longer drips from the frame plunge the now "gelatinized frame" into ice-cold water and leave it there to "set" for five or ten minutes. It would seem sufficient that the temperature of the water should be merely just below the melting-point of the gelatin solution used, but it is safest and most satisfactory to have the temperature as nearly as possible at 0° C. The writer keeps blocks of ice floating in the water to insure this.

5. Raise the "gelatinized frame" from the water and test it for leaks by filling it with ice-cold water. Water warm enough to melt the gelatin, or even to soften it, may at once create flaws, in the very process of testing itself.

6. If no flaws are discovered, plunge the "gelatinized frame" into ice-cold formalin (40 per cent.) and transfer the formalin to an ice-chest where it should remain until, by the action of the formalin, the gelatin is rendered completely insoluble in boiling water. Two weeks' time has proven entirely satisfactory for this purpose. Perhaps less time may be found sufficient.

7. Wash the now completed membrane in running water, or boil it, or steam it in free steam or in steam under pressure, to get rid of the free formalin adherent to the gelatin.

If at step 5, flaws are found (there should be none, however, if ordinary care be taken), it is best to return the "frame" to the hot gelatin solution and leave it there for ten or fifteen minutes more, at or near 100° C., to remelt the gelatin already cooled upon it, and reimpregnate the whole silk tissue. Patching flaws found in cold gelatin films with hot gelatin is not likely to yield satisfactory results.

The essentials of success are, the writer believes, first, fine, rigid meshes in the "frame;" second, close, firm, rigid seams, if the "frame" is sewed at any point; third, thorough impregnation with hot gelatin; fourth, ice-cold temperatures for the water used in setting and testing and for the formalin used in hardening; fifth, sufficient time for the formalin to act thoroughly on the gelatin. The writer has used Gold Label Brand gelatin, Comte Fils, Magdebourg, but any good sheet gelatin would probably be satisfactory.

BOARD OF HEALTH, BACTERIOLOGICAL
LABORATORY, BOSTON.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES, COLUMBIA UNIVERSITY, NO. 108.]

COMPARATIVE EXPERIMENTS UPON CHEMICAL PRESERVATIVES IN MILK.

BY H. C. SHERMAN, A. W. HAHN, AND A. J. METTLER.

Received July 16, 1905.

IN CONNECTION with other studies concerning the composition and analysis of milk, experiments upon the detection and determination, efficiency, and mode of action of chemical preservatives have been undertaken in this laboratory. The destruction of lactose and the development of acidity under the influence of sodium fluoride, sodium salicylate, and a mixture of boric acid and borax, together with notes on the determination of these com-

pounds and preliminary results obtained with hydrogen peroxide as a milk preservative are given in this paper.

For the sake of brevity the results are tabulated without detailed descriptions of individual experiments and without regard to the chronological order in which they were obtained.

DESTRUCTION OF LACTOSE AND FORMATION OF ACIDS.

The milk used in each experiment of the first series was a portion of the mixed product of about 500 cows, handled under good sanitary conditions, mixed, divided, and treated with the preservatives in previously sterilized bottles within two hours after being drawn from the udder. Each bottle was then tightly stoppered and kept at room temperature (20 to 25°). In this series each sample was

TABLE A.—DESTRUCTION OF LACTOSE AND FORMATION OF ACIDS IN SAMPLES KEPT STOPPERED.

	Lactose.		Acidity calculated as lactic acid.			
			Total (*b*).		After boiling (*c*).	
Description of sample.	Remaining. Per ct.	Destroyed (*a*). Per ct.	Per ct.	*a*:*b*::100:	Per ct.	*a*:*c*::100:
First experiment, 4 days:						
Milk with no preservative.....	3.43	1.28	0.864	67.5	0.66	51.5
Same (second bottle).....	3.43	1.28	0.86	67.0	0.65	51.0
Same milk +0.1 per cent. sodium fluoride.....	3.68	1.03	0.65	63.0	0.43	42.0
Same milk +0.1 per cent. sodium salicylate.....	3.71	1.00	0.71	71.0	0.51	51.0
Same milk +0.1 per cent. of boric acid and borax (1:1)..	3.43	1.28	0.864	67.5	0.74	58.0
Second experiment, 4 weeks:						
Milk with no preservative.....	2.93	1.80	1.24	69.0	0.99	55.0
Same (second bottle).....	2.91	1.82	1.23	67.5	0.92	51.0
Same (third bottle).....	3.02	1.71	1.25	73.1	1.03	60.0
Same milk +0.1 per cent. sodium fluoride.....	3.26	1.47	0.87	59.0	0.72	42.0
Same milk +0.1 per cent. sodium salicylate.....	3.43	1.30	1.00	77.0	0.87	67.0
Same milk +0.1 per cent. of boric acid and borax (1:1)..	3.19	1.54	0.77	77.0	1.05	68.0
Third experiment, 8 weeks:						
Milk with no preservative.....	2.52	2.25	1.59	70.0	1.39	62.0
Same (second bottle)	2.57	2.20	1.63	74.0	1.44	65.0
Same milk +0.1 per cent. sodium fluoride..	3.19	1.58	1.11	70.0	0.82	52.0
Same milk +0.1 per cent. sodium salicylate.....	3.35	1.42	1.19	84.0	0.92	65.0
Same milk +0.1 per cent. of boric acid and borax (1:1)..	2.65	2.12	1.52	72.0	1.35	64.0

always allowed to remain entirely undisturbed until the day upon which the analysis was to be made, when it was well shaken, opened, and examined for percentage of lactose, total acidity, and acidity after diluting with water and boiling gently for ten minutes to expel carbonic acid.

This series includes three distinct experiments made during April to June. The original percentages of lactose found for the three lots of milk were 4.71, 4.73, and 4.77 respectively. The results obtained in these three experiments are given in Table A.

The results given in Table A show that the milk, when treated with 0.1 per cent. of sodium fluoride or sodium salicylate and then kept in stoppered bottles, lost less lactose and developed less acidity than when kept under the same conditions without preservative or with 0.1 per cent. of a mixture of boric acid and borax. In these experiments, the shortest of which was four days long, the preservative effect of the boric acid and borax was scarcely perceptible. The influence of this preservative is shown in later experiments in which the acidity was determined daily (Table C). The results of two experiments, comparing the effect of fluoride and salicylate in milk not kept closed throughout the experimental period, are given in Table B.

These results show less uniformity than those obtained in the experiments in which the bottles were kept tightly stoppered throughout. While both fluoride and salicylate evidently retard lactic acid fermentation to a considerable extent, it is probable that other acid-forming organisms, entering the milk from the air or from the apparatus used in mixing and in withdrawing portions for analysis, were affected differently in the different samples; both directly by the kind and amount of preservative present, and indirectly through the influence of the preservative in retarding the growth of the bacteria originally contained in the milk.

In the samples kept stoppered, equal weights of fluoride and salicylate were about equally efficient in retarding the destruction of lactose and the development of acidity, but the nature of the fermentation, as indicated by the ratio of lactose used to acid formed, was affected differently in the two cases. Using as a basis for comparison the samples to which no preservative was added, it appears that the fluoride so altered the fermentation that a smaller amount of total acid was formed in the destruction of a given amount of lactose, while the salicylate had the opposite

TABLE B.—DESTRUCTION OF LACTOSE AND FORMATION OF ACIDS IN OPENED SAMPLES.

Description of sample.	Lactose. Remaining. Per ct.	Lactose. Destroyed (*a*). Per ct.	Acidity calculated as lactic acid. Total (*b*). Per ct.	Total (*b*). *a*:*b* 100.	After boiling (*c*). Per ct.	After boiling (*c*). *a*:*c* 100.
First experiment, 3–4 weeks:						
Milk[1] with no preservative when first opened	.....	.....	0.90	...	0.74	...
Four days later	2.85	1.96	1.03	53	0.81	41
Same milk +0.1 per cent. sodium fluoride when first opened	.....	.....	0.68	...	0.50	...
Four days later	3.26	1.55	0.89	57	0.63	41
Same milk +0.1 per cent. sodium salicylate when first opened	.....	.....	0.76	...	0.70	...
Four days later	3.04	1.77	0.76	43	0.72	41
Second experiment, 4 weeks: Samples opened frequently.						
Milk[2] with no preservative	2.83	1.92[2]	1.01	53[2]	0.81	42[2]
Same (second bottle)	2.85	1.90	0.95	50	0.80	42
Same milk with sodium fluoride, 0.1 per cent	2.95	1.80	0.68	38	0.57	32
Same milk with sodium fluoride, 0.02 per cent	2 30	2.45	1.54	63	1.20	49
Same milk with sodium fluoride, 0.005 per cent	3.00	1.75	0.81	46	0.63	36
Same milk with sodium salicylate, 0.1 per cent	2.83	1.92	0.86	45	0.71	37
Same milk with sodium salicylate, 0.02 per cent	2.30	2.45	1.11	45	0.83	34
Same milk with sodium salicylate, 0.005 per cent	2.06	2.69	1.25	46	0.96	36

effect. In the samples which were exposed to the air, these relations are sometimes reversed. The irregularities are especially marked in the samples containing only small amounts of preservatives.

INFLUENCE OF AMOUNT OF PRESERVATIVE UPON THE DEVELOPMENT OF ACIDITY.

Two series of experiments with different amounts of preserva-

[1] From same source, and treated in same manner to time of first opening, as the milk used in the preceding experiments. Lactose originally present 4.81 per cent.

[2] This milk was from a different source, was inferior to that previously used, and was between one and two days old when the experiment was begun, having been obtained from a restaurant. As the determination of lactose in the original sample was accidently omitted, it is assumed that 4.75 per cent. was present.

tives were carried out, the first comparing sodium fluoride and sodium salicylate, the second comparing hydrogen peroxide and the mixture of equal parts borax and boric acid. In each case the milk used was obtained in a restaurant and was probably 1 to 2 days old at the beginning of the experiment.

In determining total acidity, 10 cc. of milk were diluted to 100 cc. and titrated with tenth-normal sodium hydroxide, using phenolphthalein as indicator. For acidity after boiling, 10 cc. were diluted in the same way and the mixture boiled gently for ten minutes in a beaker loosely covered with a watch-glass, cooled to room temperature, and titrated exactly as in the determination of total acidity. Table C gives the results of these determinations, the actual volumes of alkali used in each titration being given under the heading "degree of acidity." While the arrangement of the experiments was similar for the two series, they were carried out independently upon different lots of milk.

As would be expected in view of the fact that these samples were opened frequently to remove portions for analysis, the results are somewhat irregular, especially in those cases in which small amounts of the preservatives were used. In some of these samples there is at first a retardation, but afterward a rapid increase in acidity to an amount greater than that found where no preservative was added. In all cases where 0.1 per cent. of preservative was added, its retarding effect upon the development of acidity was permanent throughout the continuance of the experiment.

The results obtained in the absence of preservatives agree with those of Van Slyke and Hart[1] in showing a sudden check to the acid fermentation after four to six days at room temperature, when a degree of acidity equivalent to 0.7 to 1.0 per cent. of lactic acid had been reached, and about 28 per cent. of the original lactose had disappeared. Beyond this point the fermentation proceeded slowly, samples kept stoppered for eight weeks showing acidity equivalent to 1.6 per cent. of lactic acid and a loss of 47 per cent. of the lactose originally present. Both of the latter figures were exceeded in some of the samples which received very small amounts of preservatives and were frequently opened for analysis.

[1] *Am. Chem. J.*, **32**, 145.

TABLE C.—INFLUENCE OF THE KIND AND AMOUNT OF PRESERVATIVE UPON THE DEVELOPMENT OF ACIDITY IN MILK.

"Degrees of Acidity"—Cubic centimeters of tenth-normal alkali to neutralize 10 cc. of milk.

Description of sample.	After 1 day.		After 2 days.		After 4 days.		After 6 days.		After 8 days.		After 11 days.		After 13 days.		After 20 days.		Remarks.
	Total.	After boiling.	Total.	After boiling.	Total.	After boiling.	Total.	After boiling.	Total.	After boiling.	Total.	After boiling.	Total.	After boiling.	Total.	After boiling.	
First Series (A. W. Hahn):																	
Milk with no preservative	2.0	1.45	6.35	5.7	10.1	8.1	10.8	8.20	10.7	9.0	11.2	8.9	11.0	9.0	11.2	9.0	Curdled within 2 days.
Same (second bottle)...	2.0	1.45	6.25	5.5	10.5	7.8	10.9	8.35	10.7	9.3	10.5	9.3	10.7	9.3	10.5	8.9	" " 2 "
Same milk + sodium fluoride:																	
0.1 per cent (1:1000)	1.65	1.20	5.7	4.9	6.9	4.9	7.6	5.5	7.7	5.5	7.5	6.7	7.5	6.3	9.1	6.75	" " 2 "
0.02 " (1:5000)	1.9	1.45	6.0	4.6	9.3	7.3	9.5	6 9	10.6	8.6	13.1	10.8	14.2	12.6	17.1	13.3	" " 2 "
0.005 " (1:20,000)	2.0	1.4	6.0	4.4	8.5	6.5	9.0	6.5	8.8	7.2	8.9	7.1	8.7	7.8	9.0	7.0	" " 2 "
Same milk + sodium salicylate:																	
0.1 per cent (1:1000)	1.6	1.1	2.9	2.2	6.2	4.1	8.0	5.1	7.9	5.9	8.7	8.4	9.0	7.1	9.5	7.9	Curdled after 6 days.
0.02 " (1:5000)	1.9	1.25	5.8	3.95	9.7	6.5	10.8	7.9	10.7	8.6	10.7	9.1	11.5	9.5	12.3	9.2	" within 2 days.
0.005 " (1:20,000)	1.85	1.25	6.0	3.9	13.1	7.8	11.3	8.1	10.6	9.4	10.2	8.5	10.7	9.0	11.6	8.2	" " 2 "
Second Series (A. J. Mettler):					After 3 days.		After 4 days.		After 5 days.		After 7 days.		After 9 days.				
Milk with no preservative	2.15	1.8	5.0	3.5	6.6	5.6	7.9	5.9	8.4	6.5	8.55	6.2	8.5	6.3			Curdled in 2 to 3 days.
Same (second bottle) ..	2.2	1.8	4.95	3.45	6.6	5.6	7.8	5.9	8.3	6.1	8.5	6.15	8.3	6.2			" " 2 " 3 "
Same milk + boric acid and borax:																	
0.1 per cent (1:1000)	1.9	1.5	2.85	2.4	4.4	3.1	6.8	4.85	7.1	5.9	7.7	6.2	7.9	6.2			" " 4 " 5 "
0.02 " (1:5000)	1.95	1.6	4.5	3.05	7.25	5.7	8.0	6.2	8.3	6.4	8.1	6.1	8.4	6.25			" " 2 " 3 "
0.005 " (1:20,000)	2.15	1.75	4.9	3.25	7.0	5.4	7.6	5.5	8.1	6.0	8.3	6.1	8.4	6.2			" " 2 " 3 "
Same milk + hydrogen peroxide:																	
0.1 per cent (1:1000)	1.5	1.1	1.85	1.45	3.25	2.65	5.2	4.1	6.8	4.9	7.3	5.6	7.7	5.8			" " 7 days.
0.02 " (1:5000)	1.6	1.25	2.9	2.4	5.5	3.65	7.3	6.0	7.8	5.4	8.25	6.1	8.0	6.1			" " 4 "
0.005 " (1:20,000)	1.8	1.4	4.2	3.0	6.4	4.4	7.5	6.1	8.25	6.8	8.3	6.0	8.4	6.1			" " 3 to 4 days.

DETERMINATION OF PRESERVATIVES.

Boric Acid.—Thompson's method[1] was used for the determination of boric acid in milk to which a mixture of crystallized boric acid and borax had been added with the following results (A. J. M.):

	I. Per cent.	II. Per cent.
Total boric acid added	0.1116	0.0104
Total boric acid found	0.1101	0.0099
	0.1095	0.0097

Sodium Fluoride.—Good results were obtained when 100 cc. of milk were mixed with 1 gram of sodium carbonate, evaporated, burned to ash, leached thoroughly with hot water, nearly neutralized with sulphuric acid, and the determination completed by Rose's method as modified by Treadwell and Koch.[2] In a sample containing 0.1 per cent. of fluoride, 94 per cent. of the amount added was found. When the addition of sodium carbonate before ignition was omitted only 2 per cent. of the fluoride originally present was recovered in the ash (A. W. H.).

Sodium Salicylate.—Attempts to recover the salicylic acid after precipitation of proteids by mercuric nitrate gave very low results, and distillation with steam is much too slow for a practical method. The following modification of Remont's method was found fairly satisfactory. To 20 cc. of milk in a separatory funnel or cylinder, add five drops of 50 per cent. sulphuric acid and shake well to break up the curd, add 25 cc. of ether, mix thoroughly, and allow to stand until the layers separate. Withdraw 5 cc. of the ether solution, evaporate in a test-tube, and boil the residue with 10 cc. of 40 per cent. alcohol, allow to cool, adjust the volume to 10 cc., and filter. To 5 cc. of the filtrate, corresponding to 2 cc. of milk, add 2 cc. of a 2 per cent. solution of ferric chloride, dilute the solution if necessary, and match the color against that developed in a solution containing a known amount of salicylic acid. After practice, it was found possible to determine salicylic acid (present as sodium salicylate, 0.1 to 0.2 per cent.) with a probable error of about 5 per cent. (A. W. H.)

Hydrogen Peroxide.—This was determined as follows:[3] To 40 cc.

[1] *Analyst*, **21**, 64 (1896). The tenth-normal alkali used for titration was freshly standardized against crystallized boric acid.

[2] *Z. anal. Chem.*, **43**, 469 (1904).

[3] Modification of the method used by Chick: *Centrbl. Bacteriol. u. Parasitenk.*, II Abth. 1901, **1**, 705.

of water, 0.5 gram of potassium iodide, and 10 cc. of 12 per cent. sulphuric acid in a flask, having projecting lip and ground glass stopper, add 10 cc. of the milk, stopper, fill the gutter formed by the projecting lip with a solution of potassium iodide to prevent any possible loss of iodine, and allow to stand in a cool dark place for two and one-half hours. Finally titrate the iodine (set free according to the reaction $2KI + H_2O_2 + H_2SO_4 = K_2SO_4 + I_2 + H_2O$) with fiftieth-normal sodium thiosulphate. It is unnecessary to use starch as indicator, since the disappearance of the yellow color produced by the action of the iodine upon the proteids affords a satisfactory end-point. Test analyses gave results about 3 per cent. too low, doubtless because of the absorption of iodine by the milk fat. Error from this cause could be avoided by curdling the milk and working upon a measured amount of filtrate, but this seems inadvisable in view of the fact that some of the peroxide might be decomposed during filtration. On account of the rapid decomposition of hydrogen peroxide in milk the amount found by analysis will always be less than that added.

Thus in an experiment in which 1 : 1000 was added, 93 per cent. of this amount disappeared within twenty-four hours (A. J. M.).

We hope to study further the determination and rate of disappearance of hydrogen peroxide in milk.

SUMMARY.

Milk kept at 20 to 25° without preservative showed a rapid increase in acidity and decrease in percentage of milk-sugar during the first three to six days, after which the acid fermentation proceeded much more slowly, but neither the destruction of lactose nor the formation of acid had ceased entirely after four weeks.

Hydrogen peroxide, sodium fluoride, sodium salicylate, and a mixture of equal parts boric acid and borax were each found to diminish distinctly the development of acidity in milk, when added in the proportion of 1 : 1000.

When present in about this proportion, any one of the preservatives can be determined quantitatively with a probable error of 1 to 6 per cent. of the amount in the milk. In the case of hydrogen peroxide, however, the preservative disappears so rapidly that the amount found present gives little indication of the quantity originally added.

In the presence of fluoride or salicylate the fermentation is

changed qualitatively as shown by the ratio of acid formed to lactose destroyed. With these preservatives it was found that occasional exposure of the samples to air, especially when the quantity of preservative present was small, led to irregular results, the final acidity sometimes exceeding that in the control samples to which no preservative had been added.

In the experiment with samples preserved by boric acid and borax or by hydrogen peroxide such irregularities did not appear. The boron preservative had no apparent influence upon the nature of the acid fermentation. The experiments with hydrogen peroxide are only preliminary.

Experiments upon the development of ammonia in milk under the influence of these preservatives and a further study of hydrogen peroxide are being undertaken in this laboratory. Discussion of the effects of preservatives upon the wholesomeness of milk will be deferred until the completion of these and other experiments.

NEW YORK, July, 1905.

TESTING WHEAT FLOUR FOR COMMERCIAL PURPOSES.

BY HARRY SNYDER.

Received June 21, 1905.

AT PRESENT no standards have been adopted by either commercial bodies or chemists for the purpose of determining the commercial value of wheat flour. The United States Department of Agriculture, however, has adopted standards as to purity and for the purpose of detecting adulterations. Various attempts have been made to adapt chemical and allied tests to purposes of determining the commercial value of flour, but, owing to the complex nature of wheat flour, none of these tests have been found to be generally applicable.

When wheat is subjected to the roller process of milling, different grades of flour are secured, as first and second patents, straight grade, and first and second clear, also "Red dog," which is sometimes used as human food but is more extensively used for animal-feeding purposes.[1]

As is well known, different kinds of wheat make distinct types of flour, which have different values for bread-making purposes, and wheat grown in the same locality during different years may,

[1] U. S. Dept. Agr., Office of Experiment Stations, Bull. 101, pp. 7–8.

owing to variations in climatic conditions, show wide ranges in bread-making value.

In the testing of flour it frequently happens that two samples have practically the same percentage of proteids but decidedly different values for bread-making purposes, and that flours of lower proteid content produce better bread than those of higher proteid content. A few examples bearing upon this point, taken from the work of the Minnesota Agricultural Experiment Station,[1] are here given:

No.	Grade of flour.	Protein. Per cent.	Size of loaf. Inches.	Commercial. rank.
94	First patent	13.19	29×26.25	1
86	" "	13.34	28½×25½	2
106	" "	14.47	28.6×24.75	2
110	" "	13.17	28.6×25.25	1
82	Second "	14.15	28.5×25.5	5
111	" "	15.32	28×25	9
22	First "	12.63	29.1×26	1
15	Second "	14.44	28.5×25	9

The determinations that have given the best satisfaction in flour-testing are moisture, ash, total nitrogen, gliadin nitrogen, granulation, absorptive capacity, and color.

The ash determination is exceedingly useful in establishing the commercial grade of flour. The first and second grades of patent flour, for example, invariably contain less than 0.48 per cent. of ash; in case a flour contains 0.5 per cent. of ash, it would not be entitled to rank with the patent grades. Straight grade flour rarely contains more than 0.55 per cent. of ash, while the first and second clear grades contain higher amounts, 0.8 and 1.75 per cent. respectively. Many of the standard brands of flour found on the market are made by combining different percentage amounts of the standard grades, and this is one reason why there is such a large difference in flours made from the same types of wheat. Data in regard to the relation of ash to grade of flour will be found in the bulletins of the Minnesota Experiment Station.[2]

The determination of moisture is especially helpful as an indication of the keeping qualities of the flour, as an excessive moisture content, above 13, has a tendency to induce fermentation changes. Flours of the best bread-making qualities contain

[1] Minn. Agr. Expt. Station, Bull. 85, pp. 202–210.

[2] Minn. Agr. Expt. Station, Bulls. 85 and 90; also Bulletins of the U. S. Dept. of Agr., Office of Expt. Stations, Nos. 101 and 126.

11.5 to 13 per cent. of proteid material (N×6.25). The nitrogen content of flour is, however, only a general index of bread-making value. A low nitrogen content, less than 1.5 per cent., indicates deficiency in gluten, and this results in a lower absorptive capacity of the flour, lack of expansion in the loaf, and poorer physical properties of the bread. Flours containing more than 12.5 or 13 per cent. of proteid materials do not, as a rule, have improved bread-making values, as an excessive amount of gluten does not appear to be beneficial for bread-making purposes. Extensive data upon this point will be found in the bulletins previously quoted. The composition of proteids or glutinous material has more influence upon the bread-making value of flour than has the total amount of proteids. Since the principal proteids of wheat flour are gliadin and glutenin, it is believed by many that the ratio in which these two proteids are present determines largely the value of the glutinous material for bread-making purposes. The work that has been done in this line shows that with flours milled from sound normal wheats there is a definite relation of gliadin to glutenin, and that either an excessive or a scant amount of gliadin will give abnormal bread-making qualities to flour. Girard, Guthrie and others have attempted to determine the ratio which gliadin should bear to glutenin for bread-making purposes. The work done in this direction indicates that the gliadin percentages of flour from wheats of different years and produced under different conditions are subject to material variations. The author has found that during some years as high as 70 per cent. of the total nitrogenous material of wheat is soluble in 70 per cent. alcohol, while in other years flour from wheat grown under similar conditions contains as low as 45 per cent. of its proteids soluble in 70 per cent. alcohol, and that these differences have been associated with only minor variations in the size of the loaf or general bread-making value of the flour.

The gliadin determination, however, has been found very helpful in determining abnormal conditions in the composition of wheats, and the results available at the present time indicate that the percentage amount of gliadin in a flour is of more importance than the gliadin-glutenin ratio. In comparing different grades of flour milled from the same wheat, differences are observed in the gliadin percentage, the lower grades of flour having a tendency to contain proportionately less gliadin than the higher

grades. In the investigation conducted at the Minnesota Experiment Station on the 1902 wheat crop, it was found that the clear grades of flour contained nearly 4 per cent. more proteids than the patent grades, but that the percentage of total nitrogen in the form of gliadin was about 7 per cent. lower than was found in the patent grades, which made a loaf 4 inches larger and of better physical qualities than the clear grades.

	Ash. Per ct.	Protein. Per ct.	Gliadin. No.	Acidity. Per. ct.	Size of loaf. Inches.	Commercial rank.
Average of 11 tests, Mill 1:						
First patent flour	0.39	13.56	59.07	0.07	28.62×25.32	I
Second patent flour	0.47	14.70	56.25	0.08	28.67×25.72	II
Clear grade flour	0.84	17.27	54.21	0.12	24.29×21.09	III
Average of 8 tests, Mill 2:						
Patent	0.44	15.05	58.33	0.09	29.47×26.42	I
Clear	0.82	18.01	54.88	0.14	24.29×20.83	III
Average of 14 tests, Mill 3:						
First patent	0.35	12.90	58.28	0.09	28.51×25.39	I
Second patent	0.46	14.17	56.20	0.10	28.62×25.31	II
Clear	0.86	17.01	50.03	0.15	23.91×20.43	III

In the study of the gliadin content of wheat and flour, the author has found that any slight increase in the acidity of the grain materially influences the gliadin percentage, and this undoubtedly accounts in part for the variable results that have been secured. The gliadin from different types of flour has not been found as uniform in composition as could be desired. Differences of 1 per cent. or more have been observed in the nitrogen content of gliadin from different wheats milled under similar conditions. This suggests that gliadin is lacking in definite chemical composition. Whether this is due to wheat flour containing more than one proteid soluble in 70 per cent. alcohol or to other causes the author is not prepared to say, but from the results obtained it is evident that wheat gliadin obtained under similar conditions from different types of wheat and flour is not as constant in chemical composition or physical properties as would be expected of a definite chemical compound. Consequently, the general application of gliadin results is necessarily restricted.

Various attempts have been made to assign to wheat and flour a commercial value proportional to its nitrogen content.[1] A literal interpretation of the nitrogen results would then mean that

[1] A. D. Hall: *Journal Board of Agriculture*, London, pp. 321–333.

the lower grades of flour, as first and second clear and red dog, would have a higher bread-making value than the patent grades of flour, which, of course, is an erroneous conclusion. Neither is it possible to assign to flours of the same grade a comparative value on the basis of the nitrogen determination alone, because, as previously noted, two patent flours may have the same nitrogen content and possess entirely different bread-making values. While a large amount of work has been done in studying the wheat proteids, the unique properties which give to wheat flour its high bread-making value are but imperfectly understood.

A number of fermentation changes induced by enzymes take place in wheat after it is harvested and when stored in elevators, and these changes affect the bread-making value of the flour.

The amount of acid in combination with the wheat proteids and the degree of hydration of the proteids are undoubtedly factors which materially influence the bread-making value of flours, but as yet no methods have been devised for accurately determining either acidity or hydration.

In commercial transactions color is one of the main factors in determining flour value, as each type of wheat has a tendency to produce flour of a distinct shade. Hard Northwestern wheat produces flours of a creamy tinge, while some of the soft winter wheats produce white flours. Dark-colored flours invariably possess poor bread-making qualities. The fact that color is such an important factor in determining the commercial value of a flour has resulted in the use of artificial means of bleaching. Various bleaching agents, as oxides of nitrogen and ozone, are used. A favorite way of producing the oxidizing gases is by electrical action, the flour being brought into contact with the gases thus produced. Some of the claims made for the bleaching of flour are, from a chemical point of view, most interesting, one being that by means of electrical action the amount of proteid material in flour can be largely increased by changing the starch to proteids, thereby improving the bread-making and nutritive value of the flour! This alleged method of converting starch into gluten by electrical action, although covered by United States patents, results in producing flour with practically the same nitrogen and gluten content as prior to bleaching. The main effect of bleaching is a slight change in color. In the case of flours of high color, this has been found to be a commercial advantage, as the

treated flours have a color, more like the best commercial grades. The bleaching of flour has been found to have but little influence upon the bread-making value. If, however, the bleaching is carried to excess, the proteids are slightly oxidized and the size of the loaf is decreased. It is not possible to improve the lower grades of flour, as first and second clear and red dog, so that they have the same bread-making value as patent flours. The bleaching of the lower grades and then blending them with the patents can readily be detected by the high ash percentage. The extent to which flour bleaching will be adopted remains to be determined.

Much reliance has been placed heretofore upon color in the commercial grading of flour, but the advent of bleaching renders the factor of color of minor importance in determining the grade to which a flour belongs. By the application of chemical tests, it is possible to ascertain accurately whether a flour is patent, straight or clear, but as yet chemical tests are not capable of accurately determining the bread-making value of a flour. They often indicate, however, why a flour is deficient in desirable bread-making characteristics, and from the chemical tests ways are suggested for improving the flour, but the actual bread-making value can be determined only by comparative bread-making tests. Such tests necessitate the making of the flour into bread under definite and uniform conditions, the various ingredients, as flour, yeast, salt, sugar, shortening, etc., being exactly proportioned and the fermentation and mechanical manipulations being carried on under standard and uniform conditions. For purposes of comparison, a flour of known bread-making value is used. Comparisons are made as to size of loaf, texture and other physical properties. From these comparative tests, the bread-making value of a flour can be accurately determined, including such data as the number of loaves per barrel.

In the testing of flour the best results are secured by the joint application of chemical and baking tests. When only baking tests are employed, the blending of grades cannot be readily detected, as they afford no absolute data upon which definite conclusions as to grade can be drawn, and, on the other hand, the chemical data alone are not always a safe index as to the bread-making value of the flour. In the interpretation of the results of both chemical and baking tests, no hard and fast rules can be formulated. The various factors must be separately considered

and then carefully balanced in order to secure results that are of value. It is important to note that the same factors which impart commercial value to flour are in a general way in harmony with those which impart nutritive value. The flours which make the best bread are those which are well milled and are free from fibrous offals, and these are the flours which give the low ash content. They are also mediumly rich in proteids, which impart desirable physical properties and insure a loaf of the highest value. The best commercial grades of flour are of mediumly fine granulation in contradistinction to graham and whole wheat flours. Fine granulation insures more complete digestion and absorption of the nutrients of the flour by the body.[1]

[FROM THE DEPARTMENT OF EXPERIMENTAL MEDICINE, PARKE, DAVIS & CO., DETROIT, MICH.]

ADRENALIN, THE ACTIVE PRINCIPLE OF THE SUPRARENAL GLANDS.*

BY T. B. ALDRICH.

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THE OBJECT of this paper is to take up the chemical side of adrenalin, the active principle of the suprarenal glands, but, before doing so, I will review very briefly this subject up until the time when adrenalin was discovered.

Addison[1]† (1855) was the first to recognize the great importance of the suprarenal glands in the animal economy, particularly in their relation to the disease since called "Addison's Disease."

Vulpian[2] (1856) observed that the expressed juice of these glands, obtained from various animals, gave certain characteristic color reactions, not given by any other glands in the body; for example, ferric chloride gave a green color, while iodine gave a pink or rose-red color.

Virchow[3] (1857) substantiated Vulpian's observations, but added nothing new of importance.

Vulpian and Cloez[4] (1857), Arnold[5] (1866), and Holm[6] (1867), attempted the isolation of the active principle, but were unsuccessful.

[1] Office of Experiment Stations, U. S. Dept. of Agriculture, Bulls. 101 and 126.

* Read before the Section of Physiology, at the Buffalo Meeting of the American Chemical Society, June 23, 1905.

† The numbers refer to the literature at the end of the article.

Krukenberg[7] (1885) called attention to the similarity of the color reactions of the extract and those of pyrocatechol. He endeavored to isolate the active principle according to Arnold's method. A body was obtained and analyzed, but no formula was proposed.

Brunner[8] (1892) confirmed Krukenberg's work, in reference to the similarity of the color reaction of pyrocatechol and the active principle.

Oliver and Schafer[9] (1894) made the important discovery that the extract produced a rise in blood-pressure when injected intravenously.

Moore[10] (1895) found that the reducing property and the ability to raise the blood-pressure went hand in hand, and concluded that the physiologically active body is identical with the reducing body which gives the green color reaction with ferric chloride.

Frankel[11] (1896) isolated a syrup-like body which he considered a pure substance. He called it "sphygmogenin," but no chemical criteria are given of its purity. It was not even shown to possess a constant composition, and no attempt was made to establish an empirical formula for it. Frankel held the active principle to be a nitrogenous pyrocatechol derivative.

Mühlmann[12] (1896) considered the active principle to be pyrocatechol.

Moore[13] (1897) held that Frankel was wrong in assuming the active principle to be a derivative of pyrocatechol, and argued rather that it was a derivative of pyridine, but of this he was not certain.

Abel and Crawford[14] (1897) showed that what they called the active principle may be precipitated from aqueous extracts of the gland with benzoyl chloride and sodium hydroxide, and that this benzoyl product may be decomposed with hot, dilute sulphuric acid. This so-called active principle was obtained in the form of a sulphate of a tarry consistency which possessed physiological activity and which gave the color and other specific reactions of the suprarenal extract.

In two subsequent papers by Abel (1898)[15], (1899)[16], the following statements among others were made in reference to the so-called active principle which he now named "epinephrin."

Epinephrin is a basic substance thrown out of its solution in acid

by ammonia in the form of an amorphous flocculent compound, which rapidly loses its power to raise the blood-pressure. It gives reactions with a number of alkaloidal reagents, the color reactions of Vulpian, reduces silver nitrate and in all other ways agrees with Vulpian's chromogen. After saponifying the benzoyl product, the liberated base may be precipitated as a picrate, and from this picrate other salts formed possessing considerable activity. $C_{17}H_{15}O_4N$ is the formula ascribed to the base. Later I will discuss the various formulas proposed by Abel from time to time for the active principle.

v. Fürth (1897)[17], (1898)[18], (1900)[19], from the analyses of an impure acetyl product, assumed the constituent which raises the blood-pressure to be either tetrahydrodioxypyridine, $C_5H_9O_2N$, or dihydrodioxypyridine, $C_5H_7O_2N$. As v. Fürth has lately abandoned this theory, no more need be said in reference to this claim. A contribution of value, however, was the isolation of what he concluded to be the active principle in the form of a physiologically active, though impure, iron compound. In the analysis of the same, he assumes by comparison with the commercial preparation, adrenalin, that those fractions of his iron compound which shows the highest percentage of carbon most nearly represent the true composition of the substance which raises the blood-pressure. To this body v. Fürth gave the name "suprarenin," claiming that it was different from epinephrin, and even going so far as to state that epinephrin itself has no connection with the active principle, but is a very different substance slightly contaminated with the true blood-pressure-raising constituent.

Up until 1900 the active principle of the suprarenal gland, as such, had not been isolated, although derivatives and salts of what they presumed to be the same, were claimed by both Abel and v. Fürth, but these compounds were no doubt either impure derivatives or products formed from a modified form of the active substance. For example, Abel assumed that his autoclave product, after saponification, was the active principle, but this later was found to be wrong, being really a monobenzoyl derivative of a modified form of the real active principle.

It was not until January, 1901, that the active principle was isolated by Takamine who gave a preliminary paper[20] before the New York Section of the Society of Chemical Industry, entitled "Adrenalin, the Active Principle of the Suprarenal Gland," and,

who in November of the same year published a more detailed article[21] on the same subject in the *American Journal of Pharmacy*. In August of 1901 the writer[22] succeeded also by a method differing slightly from that of Takamine's in isolating a body, which was shown to be identical with adrenalin. Later Aldrich[23] showed by reduction tests, and blood-pressure-raising experiments, that adrenalin is identical with the blood-pressure-raising and reducing body as found in the gland and is therefore the active principle of the same. Before the decomposition products, and the empirical and structural formulas of the active principle could be determined, it was necessary to obtain it in a fairly pure condition. To-day, however, we can make the statement that this elusive body, which baffled the efforts of a number of able investigators, has been isolated in a pure form, in comparatively large amounts, that it is an article of commerce (both as such and in solution), and that several investigators even claim to have produced the same, or bodies having the same physiological properties, synthetically.

I would like to add here that, although the investigations on this subject extend over such a long period of time, by far the greater number and the most important contributions have been made during the past few years. From 1855-1895 we find ten articles, some of which are very short, while from 1895-1905, one-fourth the time, we have upwards of thirty, dealing mainly with the isolation and chemistry of the active principle of these glands. The incentive for the increased interest in this field was no doubt in part due to the discovery of Oliver and Schafer that the extract of the gland, when injected intravenously, caused a rise of blood-pressure, and also in a very great degree to the very important discovery of Dr. Bates, of New York, that the very dilute extract possessed marked haemostatic properties. Considerable interest was also aroused in determining the empirical formula of adrenalin, its decomposition products and eventually its synthesis.

Having reviewed briefly the history of the isolation of the active principle of the suprarenal gland up to 1901, we are now brought to a discussion of the chemical side of adrenalin, but before taking up this subject, I will state briefly one method of isolation and some of the chemical and physical properties of the substance.

The glands are finely disintegrated and steeped in slightly acidulated water for a few hours at a temperature of about 70° C.

with frequent agitation. The temperature is then raised to about 95° so as to coagulate a portion of the proteid. The insoluble portion is now pressed and separated from the extract which contains most of the adrenalin, cooled and separated from the fat. This extract is now evaporated to a small volume and four or five times its volume of alcohol added, whereby more inert matter is separated. The alcoholic solution is then evaporated, preferably in a vacuum, and to this residual liquid, alkali is added, preferably ammonia until the solution is distinctly alkaline. The yellowish brown precipitate, which forms very quickly if the solution is sufficiently concentrated, is crude adrenalin which may be purified in various ways.

When pure, adrenalin is a very light yellowish micro-crystalline body, crystallizing in various forms according to the condition of the solution, etc., from which it is obtained. I have observed burrs of needles, tomato-like forms, wheat-sheaf forms (similar to tyrosine), boat-shaped forms and others. When dry it is perfectly stable. Adrenalin is a basic body, forming salts which are difficult to isolate. It is very slightly soluble in both cold and hot water, quite insoluble in the organic solvents, and gives all the characteristic color reactions of the suprarenal extract, as described by Vulpian, except in an intensified manner. Its solution reduces Fehling's solution by boiling, silver solution and gold chloride solution in the cold, etc., and does not give in general the so-called alkaloidal reactions. Furthermore, adrenalin is very susceptible to oxidation, the presence of alkalies favoring this process.

THE EMPIRICAL FORMULA OF ADRENALIN.

In one of my earlier articles[22] the results of some combustion analyses of adrenalin, prepared according to two different methods (Takamine's, Aldrich's), were given, showing that the active principles obtained by these two methods are identical. Furthermore, the empirical formula $C_9H_{13}O_3N$ was proposed as the most probable formula for adrenalin, the analytical data obtained from these combustions agreeing more closely with this formula than with any other expression that could be deduced.

Somewhat later, Takamine[21] gave $C_{10}H_{15}O_3N$ as the *probable* empirical formula of adrenalin, this being calculated from five combustion analyses of the base. In addition to these two

formulas no less than four formulas for the active principle have been proposed by Abel from time to time. These are as follows:

(1) $C_{17}H_{15}O_4N$, formerly supposed to be the formula of the active principle, called by Abel, epinephrin, later, however, proven to be a monobenzoyl derivative of a modified form of the active principle.

(2) $C_{10}H_{11}O_3N$, the formula resulting by subtracting the benzoyl residue, C_6H_5CO, from $C_{17}H_{15}O_4N$ and replacing the hydrogen. This is designated as reduced epinephrin, plain epinephrin, free epinephrin, alkaloidal epinephrin, etc.

(3) $C_{10}H_{13}O_3N$ represents the same as the preceding formula $C_{10}H_{11}O_3N$, 2 hydrogen atoms being added in order to have it agree with the analytical data of certain salts and also with the formula $C_{10}H_{13}O_3N.\frac{1}{2}H_2O$.

(4) $C_{10}H_{13}O_3N.\frac{1}{2}H_2O$, epinephrin hydrate, the formula derived from the analysis of the active principle prepared according to the ammonia method. This compound is adrenalin pure and simple. The analytical data, however, for some inexplicable reason, according to Abel, do not agree with $C_9H_{13}O_3N$.

We have then the following empirical formulas for the active principle of the suprarenal gland:

Takamine.	Abel.	Aldrich.
$C_{10}H_{15}O_3N$	(1) $C_{17}H_{15}O_4N$	$C_9H_{13}O_3N$
	(2) $C_{10}H_{11}O_3N$	
	(3) $C_{10}H_{13}O_3N$	
	(4) $C_{10}H_{13}O_3N.\frac{1}{2}H_2O$	

and the question arises, which, if any, of these formulas represents the true composition of the active principle?

The only support for the formula $C_{10}H_{15}O_3N$, proposed by Takamine, is found in his own analytical data, and these data do not agree with the above formula, as seen by the following: Average: C, 59.38; H, 7.84; N, 7.88. Calculated for $C_{10}H_{15}O_3N$: C, 60.91; H, 7.61; N, 7.11. The difference in carbon (1.5 per cent.) and nitrogen (0.7 per cent.) naturally condemns this formula.

Relative to the four formulas proposed by Abel during the past few years, only two ($C_{10}H_{13}O_3N$ and $C_{10}H_{13}O_3N.\frac{1}{2}H_2O$) deserve any attention whatever; the other two ($C_{17}H_{15}O_4N$ and $C_{10}H_{11}O_3N$) having both been abandoned by Abel himself, while Pauly and

others have shown conclusively that the formula $C_{10}H_{13}O_3N.\frac{1}{2}H_2O$ should also be abandoned.

Abel considered $C_{17}H_{15}O_4N$ to be the correct empirical formula for the active principle of the suprarenal gland until a time (1901) when he endeavored to account for certain differences between von Fürth's so-called "suprarenin," and "epinephrin." At this time he stated that: "The saponification of the benzoyl derivative of epinephrin may not have been a complete one, one benzoyl having been retained, etc., equals monobenzoyl epinephrin." This was only surmised by Abel and it was not until the appearance of my first paper[22] where the following statement is found: "If we subtract a benzoyl residue from Abel's formula for 'epinephrin,' $C_{17}H_{15}O_4N$, we obtain a formula, $C_{10}H_{11}O_3N$, which is not very far removed from that of adrenalin, $C_9H_{13}O_3N$, etc., etc.," that Abel finally became positively assured that his "epinephrin," so-called, is really a monobenzoyl derivative of the modified active principle.

After Takamine's and Aldrich's method of obtaining the true active principle from the glands became known, Abel, using practically the same method (with slight modifications), prepared adrenalin, and, after the purification of the same, and making analyses, concluded that the active substance is represented not by the formulas $C_9H_{13}O_3N$ or $C_{10}H_{15}O_3N$ but by the empirical formula $C_{10}H_{13}O_3N.\frac{1}{2}H_2O$ (epinephrin hydrate). By dissolving epinephrin hydrate in *concentrated* sulphuric acid a sulphate was obtained, the analysis of which led to the formula $(C_{10}H_{13}O_3N)_2.H_2SO_4$. Accordingly, the formula $C_{10}H_{11}O_3N$ was changed to $C_{10}H_{13}O_3N$ to bring it into conformity with this. We have then, according to Abel, $C_{10}H_{13}O_3N$ for the formula of reduced epinephrin, and $C_{10}H_{13}O_3N.\frac{1}{2}H_2O$ for the formula of epinephrin hydrate (adrenalin). Pauly having shown by his own, as well as by Abel's, investigations that there is no such compound as epinephrin hydrate, we really have but one of Abel's formulas in the discussion, *viz.*, $C_{10}H_{13}O_3N$.

The ground for assuming *even this* formula is based for the most part on the analyses of derivatives of the original so-called reduced epinephrin, these derivatives being of questionable purity. In fact some were thrown out in an amorphous condition, no doubt mixed with other substances. Furthermore, *no one* has, as yet, to

my knowledge, confirmed Abel's analytical results relative to so-called epinephrin hydrate or reduced epinephrin.

Since the analytical data given in my first paper did not agree very closely (as far as carbon is concerned) with the formula $C_9H_{13}O_3N$, my advocacy of this formula at that time was made with some reservation, knowing that my results were open to criticism; still my analytical data would not allow me to accept a formula with higher or lower carbon content. Facts which will be cited below, however, leave now no doubt of the correctness of this formula and also of my previous statements. I found later that this deficiency in carbon (about 1.0 per cent.) lay in the fact that the substance was incompletely burned. However, by burning the adrenalin with powdered copper oxide, the results were found to compare favorably with the formula $C_9H_{13}O_3N$.

Below are given the results of some combustion analyses and nitrogen determinations where the adrenalin employed was purified strictly according to the oxalate method as advocated by Abel and where it was mixed with copper oxide.

(1) 0.1663 gram substance gave 0.3611 gram CO_2 and 0.1080 gram H_2O.
(2) 0.2782 gram substance gave 0.6016 gram CO_2 and 0.1833 gram H_2O.
(3) 0.1618 gram substance gave 0.3534 gram CO_2 and 0.1092 gram H_2O.
(4) 0.2177 gram substance gave 0.4727 gram CO_2 and 0.1465 gram H_2O.
(5) 0.2393 gram substance gave 0.5184 gram CO_2 and 0.1630 gram H_2O.
(1) 0.29415 gram substance gave 20.8 cc. N at 25° and 736 mm.
(2) 0.2665 gram substance gave 18.4 cc. N at 22° and 744 mm.
(3) 0.2403 gram substance gave 16.6 cc. N at 22° and 745 mm.
(4) 0.4765 gram substance gave 32.6 cc. N at 22° and 745 mm.

	Calculated for.	Found.					Average.
	$C_9H_{13}O_3N$.	I	II	III	IV	V	
C.....	59.01	59.17	58.97	59.51	59.21	59.08	59.19
H.....	7.10	7.21	7.29	7.47	7.43	7.56	7.39
N.....	7.65	7.63	7.65	7.66	7.59	...	7.63

The formula of adrenalin, $C_9H_{13}O_3N$ (mol. wt. 183), not only finds confirmation in the analyses given above, but also in the titrations given below where the average of seven titrations gives a molecular weight of 183.7. The formulas $C_{10}H_{15}O_3N$ (Takamine), $C_{10}H_{13}O_3N$ and $C_{10}H_{13}O_3N.\frac{1}{2}H_2O$ (Abel), are not to be considered in this connection, since their molecular weights are much above that actually obtained, $C_{10}H_{15}O_3N$ requiring 197, $C_{10}H_{13}O_3N$ 195, and $C_{10}H_{13}O_3N.\frac{1}{2}H_2O$ 204.

(1) 0.3519 gram adrenalin requires 19.1 cc. N/10 H_2SO_4 to form neutral salt 183.7.

(2) 0.41495 gram adrenalin requires 22.5 cc. N/10 H_2SO_4 to form neutral salt 184.0.

(3) 0.3253 gram adrenalin requires 17.7 cc. N/10 H_2SO_4 to form neutral salt 183.3.

(4) 0.4258 gram adrenalin requires 23.3 cc. N/10 H_2SO_4 to form neutral salt 182.6.

(5) 0.2951 gram adrenalin requires 16.2 cc. N/10 H_2SO_4 to form neutral salt 182.7.

(6) 0.3568 gram adrenalin requires 19.3 cc. N/10 H_2SO_4 to form neutral salt 184.9.

(7) 0.3285 gram adrenalin requires 17.8 cc. N/10 H_2SO_4 to form neutral salt 184.3.

Average, 183.7.

My formula, $C_9H_{13}O_3N$, does not rely solely on the above for confirmation as it has during the past few years been verified through analyses by a number of investigators among whom may be mentioned v. Fürth,[25] Pauly,[26] Jowett[27] and others.[28,29] Furthermore, v. Fürth and others by molecular weight determinations have excluded the possibility of doubling the formula $C_9H_{13}O_3N$.

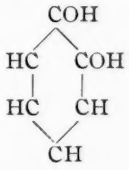
From all the foregoing it would seem that we are warranted in assuming $C_9H_{13}O_3N$ to be the correct empirical formula of adrenalin, the active principle of the suprarenal gland.

STRUCTURAL FORMULAS.

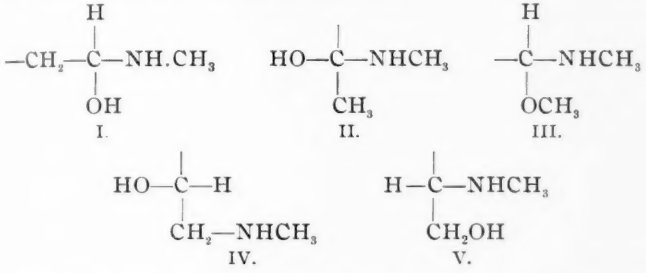
Before the active principle of the suprarenal glands had been isolated in a pure form, certain facts were observed relative to certain reactions and decomposition products, but those observed facts were of doubtful value for the reason that it was not certain whether the observed products came from the active principle or from some body or bodies with which it was associated.

As early as 1885 Krukenberg expressed his belief that the substance which gives the green color with ferric chloride is pyrocatechol, and from this time on the belief that pyrocatechol or some derivative of it is present in the glands gained a firm hold. In 1895 Moore came to the conclusion that the pyrocatechol-like body and the blood-pressure-raising body are identical. In 1901 Takamine obtained from the pure active principle, by fusing with potassium hydroxide, crystals that possessed the physical and chemical properties of pyrocatechol and protocatechuic acid.

Later v. Fürth confirmed Takamine's observations and also demonstrated with others that adrenalin contains a methylamine group and also probably three hydroxyl groups, one of which is situated outside of the ring nucleus. From his own experiments and observations v. Fürth proposed the cyclic complex



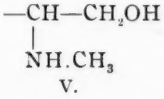
as the basis of the adrenalin molecule and Pauly,* discovering that adrenalin contains an asymmetric carbon atom, accepted the foregoing, and suggested the following five possible formulas for the side-chain in the adrenalin molecule:



I. II. III.

IV. V.

Of these five possible structural side-chains, Pauly considers IV and V to be the most probable, since they explain the formation of several decomposition-products the most satisfactorily, but V is given the preference:

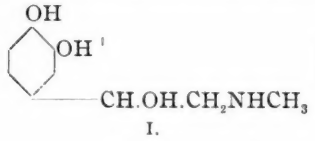


V.

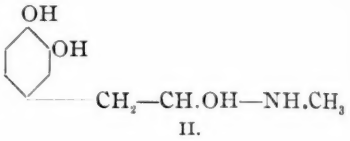
Jowett[27] confirmed the formula $C_9H_{13}O_3N$, first proposed by Aldrich, by the analysis of carefully prepared material and by molecular weight determinations. He also obtained by fusion with potassium hydroxide what he supposed to be protocatechuic acid, although he was not certain whether the presence of this

* *Ber.*, **36**, 2944 (1903).

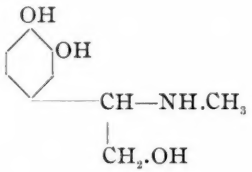
complex in the original substance could be correctly deduced from its formation. Oxalic acid, formic acid, and methylamine were also obtained by oxidation with permanganate. By thorough methylation and subsequent oxidation with permanganate, trimethylamine and veratric acid were obtained, thus proving the existence of the complexes $C_6H_3(OH)_2$—C and $NH.CH_3$ in the original base. He deduces from his results the following possible constitutional formulas for adrenalin:



I.



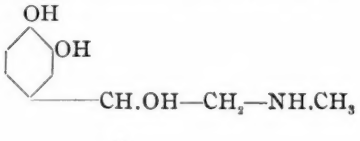
II.



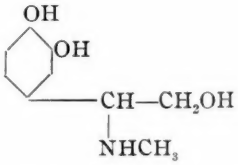
III.

Jowett considers I to be the most probable, for after methylation and subsequent oxidation of II* we would expect to obtain homoveratric acid, $C_6H_3(OCH_3)_2CH_2COOH$, whereas veratric acid, $C_6H_3(OCH_3)_2COOH$, was actually obtained. The objection to III is that it would not so readily explain the formation of pyrrol or skatol derivatives. I will add here, however, that Pauly in a later paper states that III can explain the formation of pyrrol as well as I, and that skatol should not be considered in this connection as it was not obtained from adrenalin but from benzoylepinephrin.

We have then from what has been cited the two following structural formulas for adrenalin:



I.

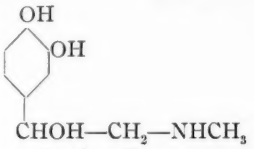


II.

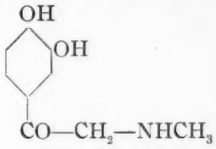
* Jowett's argument for Formula I is not entirely convincing, for II would no doubt also yield veratric acid, since it would be difficult to stop at the homoveratric stage.

As to which is the correct formula, we are unable to state positively at the present time. Evidence has been and is accumulating, however, in favor of I, still there is some evidence in favor of II.

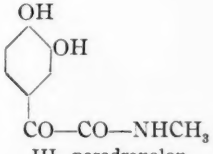
E. Friedmann* endeavored to establish the constitution of adrenalin in another manner. By oxidizing tribenzolsulphoadrenalin (described by v. Fürth), he obtained a body (adrenalon) having the same carbon content, but having no asymmetric carbon atom. It has the character of a ketone. By further oxidation, there was obtained another oxidation product (peradrenalon) with the same amount of carbon. It is to be considered a substituted acid amide. From these results it is concluded that the formula of adrenalin is represented by I, as advocated by Jowett.



I, adrenalin.

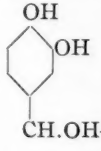


II, adrenalon.



III, peradrenalon.

Friedmann also endeavored to support the above by preparing II, adrenalon, synthetically and then forming the tribenzolsulpho body from the same. This tribenzolsulpho body is not to be distinguished from the first oxidation product obtained from tribenzolsulphoadrenalin; neither is its oxidation product different from the peradrenalon product obtained from adrenalin.

Assuming 

to be the correct constitutional formula for adrenalin, a number of investigators have endeavored, by

* *Beiträge zur chemischen Physiologie u. Pathologie*, **6**, 92, September, 1904.

starting with pyrocatechol, to prepare adrenalin synthetically, and, although their endeavors have not been entirely successful, still bodies have been obtained that have at least the qualitative physiological properties of adrenalin as well as some of the physical and chemical properties. Among those who have prepared such bodies may be mentioned Roser[31], who claims to have produced synthetic adrenalin or at least a substance acting like adrenalin. This body, methylaminorthodioxyacetophenon, was described by H. Meyer at the International Congress of Physiologists at Brussels. Qualitatively it exhibited an effect exactly like that of adrenalin, not only as far as the peripheral vaso-constricting action following intravenous injection is concerned, but also as to the action on the smooth muscular fiber and the causation of diabetes. It was further found that a series of homologous compounds (aminoketones, ethylaminoketones, etc.) exert a similar action.

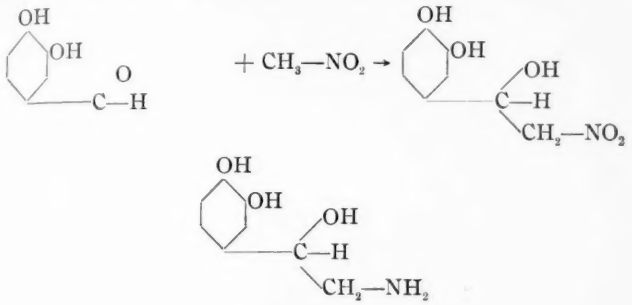
E. Friedmann[30] prepared methylaminoacetopyrocatechol (adrenalon) and found that it possessed marked physiological properties in raising the blood-pressure.

F. Stolz,[32] having convinced himself by experiment that the formula of Aldrich, $C_9H_{13}O_3N$, for adrenalin was correct, and that its degradation products were essentially as given by others, accepted the structural formulas advocated by Pauly and Jowett. Stolz prepared substances having properties similar to those of adrenalin, such as methylaminoacetopyrocatechol, which, when reduced, approached adrenalin still more closely, ethylaminoacetopyrocatechol, and aminoacetopyrocatechol. Exact identity could not be established, however.

Dakin[33] has contributed the latest article on this subject, "The Physiological Action of Synthetic Substances Allied to Adrenalin." The basic body, which was obtained from methylaminoacetopyrocatechol by reduction, differs somewhat from the native product. The salts of this base, however, show all the chemical reactions of adrenalin. Furthermore, the physiological activity of the new substance is about the same as adrenalin. This base is no doubt the same as that obtained by Stolz,* where he states: "By reduction of the alkylaminoacetopyrocatechol a compound is formed whose physiological activity approaches more closely that of adrenalin."

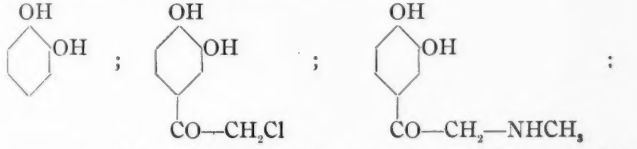
* *Ber.*, **37**, 4149.

A further attempt was made by Dakin to prepare synthetically from protocatechuic aldehyde, bodies similar to adrenalin. This was accomplished by condensing protocatechuic aldehyde with nitromethane without the elimination of water and then reducing the nitro group. The changes are represented as follows:

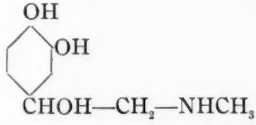


This base was found to be also physiologically active.

The original material in making all of the synthetic bodies cited above, excepting the last, is pyrocatechol from which successively chloracetopyrocatechol, methylaminoacetopyrocatechol and the reduction product of the latter are formed. The successive bodies are indicated by the following formulas:



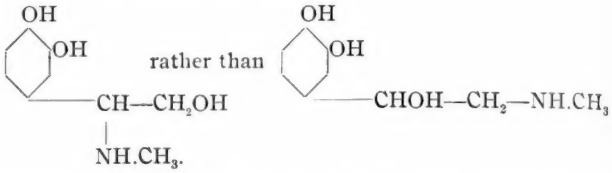
Pyrocatechol. Chloracetopyrocatechol. Methylaminoacetopyrocatechol.



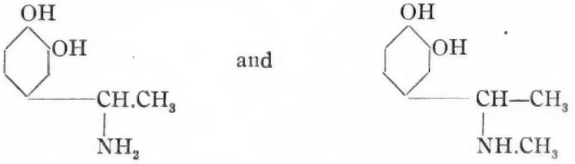
Adrenalin (?)

All the synthetic work thus far published, relative to adrenalin, is along the lines indicated above, and it has all been more or less anticipated by S. Dzierzgovsky,[34] who not only prepared chloracetopyrocatechol but dimethylaminoacetopyrocatechol and other similar bodies.

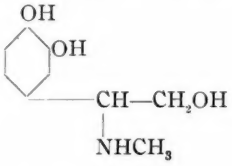
In closing, I wish to say that for some time past (since July, 1904) I have been occupied with some bodies which have been built up along the lines of the formula



Qualitatively, these bodies act in solution very similarly to adrenalin, when injected intravenously. No doubt they are represented by the formulas:



Work along this line is being carried out at the present time, and I am in hopes soon to be able to report more specifically relative to the same, also to have carried the work far enough so as to obtain the body represented by the formula:



RÉSUMÉ.

(1) Adrenalin is the native active principle of the suprarenal gland, this being shown conclusively by reduction tests and blood-pressure tests, in which a definite amount of extract was taken, divided into two equal parts and the reducing power and blood-pressure-raising power of one portion, compared with that of the adrenalin obtained from the other portion. These were found to be practically the same after making due allowance for the small amount of adrenalin that it is difficult to precipitate from the extract.

(2) From the evidence at hand none of the following formulas proposed by different authors, (Takamine) $C_{10}H_{15}O_3N$, (Abel) $C_{17}H_{15}O_4N$, $C_{10}H_{11}O_3N$, $C_{10}H_{13}O_3N$ and $C_{10}H_{13}O_3N.\frac{1}{2}H_2O$, can be accepted as representing the true composition of adrenalin.

(3) $C_9H_{13}O_3N$, the formula first proposed by Aldrich for adrenalin, represents without doubt the true composition of this body, this being shown not only by Aldrich's later analyses but also by the confirmatory analyses of v. Fürth, Pauly, Jowett, Abderholden and Bergell and Bertrand.

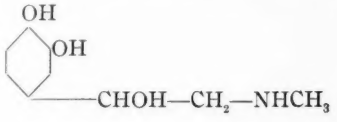
(4) The formula $C_9H_{13}O_3N$ finds also confirmation in the titration experiments cited, where the average of seven determinations gives a molecular weight of 183.7 ($C_9H_{13}O_3N$, 183).

(5) Molecular weight determinations of adrenalin and its derivatives by *physical methods* also confirm the formula $C_9H_{13}O_3N$.

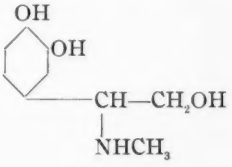
(6) Adrenalin contains undoubtedly a pyrocatechol complex, an asymmetric carbon atom, three hydroxyl groups, one being in the side-chain and a methylimide group (N—CH_3).

(7) Thorough methylation of adrenalin and subsequent oxidation gives veratric acid and trimethylamine.

(8) One of the two following formulas proposed by Pauly represents possibly the structure of the adrenalin molecule:



I.



II.

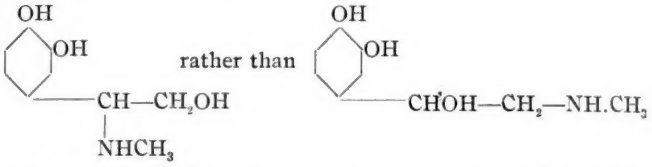
(9) It is not positively decided as yet which of the above formulas is the correct one. Preponderance of opinion seems, however, to favor I.

(10) Assuming I to be the correct formula, a number of bodies have been prepared from pyrocatechol, through chloracetopyrocatechol, by treatment with ammonia, alkylamines and other basic bodies, some of which qualitatively seem to be similar to adrenalin as regards their physiological effects.

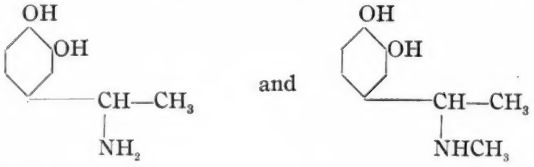
(11) Dakin has apparently obtained a body by reducing methylaminoacetopyrocatechol, whose salts show all the reactions

of natural adrenalin, but certain differences appear to exist between the free bases. The physiological activity is about the same as adrenalin.

(12) Bodies have been prepared in solution, that have been built up along the lines of the formula:

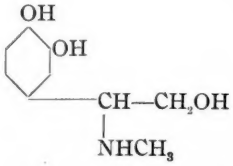


Qualitatively, these are similar to adrenalin, when injected intravenously. They are probably represented by the formulas:



respectively.

There is hope of obtaining the body represented by the following formula:



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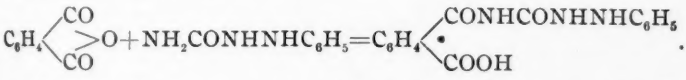
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]

THE ACTION OF PHENYLSEMICARBAZIDE AND SEMICARBAZIDE HYDROCHLORIDE ON PHTHALIC ANHYDRIDE.

BY FREDERICK L. DUNLAP.

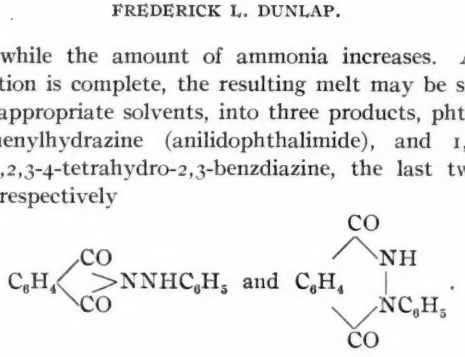
Received July 3, 1905.

WHEN phenylsemicarbazide and phthalic anhydride are heated together to 140-145°, they combine to form phthalic acid monophenylsemicarbazide as follows:



This acid decomposes on heating, carbon dioxide and small quantities of ammonia being at first evolved. As the decomposition proceeds, the amount of carbon dioxide formed gradually

decreases while the amount of ammonia increases. After the decomposition is complete, the resulting melt may be separated, by use of appropriate solvents, into three products, phthalimide, phthalylphenylhydrazine (anilidophthalimide), and 1,4-diketo-2-phenyl-1,2,3-4-tetrahydro-2,3-benzdiazine, the last two products being respectively



Phthalylphenylhydrazine has been described by a number of investigators, and of especial note is the disagreement as to the true color of this compound. Pickel[1], its discoverer, found it to be yellow. The same year that Pickel's work appeared, Hötte,[2] in a preliminary report on the action of phenylhydrazine on the anhydrides of organic acids, makes brief mention of this compound and describes it as being yellow. Pellizzari[3] found it to be straw-colored and says that in crystallizing it from alcohol, "*it can assume rather different aspects, so much so as to make one doubt whether the substance is a single compound (unico).*"[4] Just[5] has obtained this compound by a method exactly similar to Pellizzari's, but he describes it as being colorless.

In 1887, Hötte[6] published the full details of the research, the preliminary report on which had appeared the preceding year. In a foot-note in this paper,[7] he calls attention to the discrepancy in color ascribed to this compound by various investigators, and also states[8] that from alcohol, this substance crystallizes in warty aggregations of needles as well as in longer prismatic crystals. Henriques[9] describes the color as yellow, while Eibner and Merkle[10] say it is colorless. In attempting to purify the phthalylphenylhydrazine, formed during the decomposition of phthalic acid monophenylsemicarbazide, it was found that there were un-

[1] Inaugural Dissertation (Erlangen), p. 12 (1885); *Ann. Chem.* (Liebig), **232**, 232 (1886).
[2] *J. prakt. Chem.* [2], **33**, 99 (1886).
[3] *Gazz.*, **16**, 203 (1886).
[4] *Loc. cit.*, page 204.
[5] *Ber.*, **19**, 1204 (1886).
[6] *J. prakt. Chem.* [2], **35**, 265 (1887).
[7] *Ibid.*, p. 270, foot note No. 4.
[8] *Ibid.*, p. 269.
[9] *Ber.*, **21**, 1616 (1888).
[10] *Ibid.*, **35**, 2300 (1902).

questionably two bodies of different appearance present, which were unlike not only in their color but also in their crystalline habit. Unable to separate them at first by means of solvents, conditions were found under which the crystals could be obtained of sufficient size so that they could be separated mechanically. One form was white, the other being lemon-yellow. Both these compounds had the same melting-point and gave the same results on analysis, and it then became evident that it was a case of physical isomerism that was being dealt with.

A careful study of the conditions showed that the stable or yellow form may be readily produced in a number of ways and quite free from the labile or white form. For example, if a saturated glacial acetic acid solution of this compound is made at the boiling-point of the acetic acid, and then the temperature is allowed to drop a few degrees and held at this point, when crystallization takes place, it is always with the formation of the stable form, quite free from the labile; or, if either the labile or stable, or a mixture of the two, be heated with a boiling saturated solution of phthalylphenylhydrazine in alcohol, acetone, or glacial acetic acid, the undissolved part rapidly and completely passes over into the stable form. Perhaps the most satisfactory method for the production of the labile form is by crystallization from alcohol, although the labile form thus separated is seldom quite free from some of the stable.

When a boiling-hot saturated solution of phthalylphenylhydrazine in acetone is allowed to stand, the crystals separate but slowly and usually both forms are produced in crystals frequently measuring several millimeters in length. The crystals formed in this way were satisfactory for crystallographic measurement, and it has been found that the labile form crystallizes in the orthorhombic system, while the stable is monoclinic. That the two forms have the same melting-point is explained by the fact that the transition temperature of the labile into the stable lies a number of degrees below the melting-point of the stable. No satisfactory melting-point of the labile was obtained even by the dipping method.

The compound previously mentioned as 1,4-diketo-2-phenyl-1,2,3,4-tetrahydro-2,3-benzdiazine, has been previously described by Pellizzari[1] (under the name of phthalyl phenylhydrazide) and

[1] *Gazz.*, **16**, 205 (1886).

by Hötte[1] who calls it β-phthalylphenylhydrazine in contradistinction to the compound $C_6H_4\begin{matrix}CO\\ \\ CO\end{matrix}>NNHC_6H_5$, which he named α-phthalylphenylhydrazine.[2] Both Pellizzari and Hötte describe the β-compound as white, while Henriques[3] says that it is pale red. I have obtained the β-compound many times during the course of this work, and, when perfectly pure, it is always white in color.

The constitution

$$C_6H_4\begin{matrix}CONHCONHNHC_6H_5\\ \\ COOH\end{matrix}$$

has been given to the compound formed by the addition of phthalic anhydride and phenylsemicarbazide, as it best explains the formation of the various decomposition products. In the first place, when the acid is heated to its melting-point, carbon dioxide and a small amount of ammonia are produced. This first stage in the decomposition may be represented as follows:

$$C_6H_4\begin{matrix}CONH|CO|NHNHC_6H_5\\ \\ CO\quad\ |O|H\end{matrix} =$$

$$C_6H_4\begin{matrix}CO\\ \\ CO\end{matrix}>NH + CO_2 + C_6H_5NHNH_2,$$

with the formation of phthalimide, carbon dioxide and phenylhydrazine. In the first stages of the decomposition, the odor of phenylhydrazine is distinctly noticeable in the escaping gases. The next stage in the reaction is the action of the phenylhydrazine on the phthalimide:

$$C_6H_4\begin{matrix}CO\\ \\ CO\end{matrix}>NH + NH_2NHC_6H_5 = C_6H_4\begin{matrix}CO\\ \\ CO\end{matrix}>NNHC_6H_5 + NH_3.$$

That such a reaction may take place between phthalimide and phenylhydrazine, has been shown by both Just[4] and Pellizzari,[5] and I have also had occasion to verify it many times. This

[1] *J. prakt. Chem* [2], **35**, 281, 284, 290 (1887).

[2] For the sake of brevity, Hötte's nomenclature with respect to these compounds will be made use of.

[3] *Ber.*, **21**, 1617 (1888).

[4] *Ibid.*, **19**, 1204 (1886).

[5] *Gazz.*, **16**, 203 (1886).

second stage then accounts for the evolution of ammonia, and its increase as the carbon dioxide decreases, it being the later or secondary stage in the decomposition. The loss of some phenylhydrazine during the decomposition of the phthalic acid monophenylsemicarbazide, leaves the phthalimide in excess of the theoretical amount necessary to combine with the phenylhydrazine. No phenylhydrazine has been isolated from the final product, but phthalimide was readily obtained and identified by its physical properties as well as by analysis. There is still, however, one phase of this reaction to be accounted for, namely, the formation of the β-compound.

Both Just and Pellizzari in their work on the action of phenylhydrazine on phthalimide, isolated only the α-compound, yet, if the explanation of the decomposition of phthalic acid monophenylsemicarbazide as given above be correct, the only conceivable opportunity for the β-compound to form would be through the interaction of the phenylhydrazine and the phthalimide.

The work of Just and Pellizzari has been carefully repeated, and a ready explanation for the formation of the β-compound was obtained. The first stage in the interaction of these two substances is their addition with the formation of anilidophthaldiamide,

$$C_6H_4\begin{cases}CONHNHC_6H_5\\CONH_2\end{cases}.$$

On heating, this compound readily decomposes, the decomposition taking place in two ways:

$$\text{I. } C_6H_4\begin{cases}CON\ H\ NHC_6H_5\\CO\ \ NH_2\end{cases} = C_6H_4\begin{cases}CO\\CO\end{cases}>NNHC_6H_5+NH_3.$$

$$\text{II. } C_6H_4\begin{cases}CONHN\ H\ C_6H_5\\CO-\ \ NH_2\end{cases} = C_6H_4\begin{cases}CONH\\|\\CONC_6H_5\end{cases} + NH_3.$$

The first method of decomposition yields the α, while the second produces the β. The α is not formed from the β, or *vice versa*, by molecular rearrangement. The decomposition takes place mainly according to I, the β-compound always forming in smaller amounts, but both products are always formed. The constitution

assigned to phthalic acid monophenylsemicarbazide therefore explains satisfactorily all the facts obtained from the decomposition of this acid.

In studying the action of phenylhydrazine on phthalic anhydride, Pellizzari[1] obtained β-phthalylphenylhydrazine. The accuracy of Pellizzari's work was questioned by Hötte[2], for he isolated only the α-compound. In answer to Hötte, Pellizzari[3] showed that both products were formed in amounts which varied with the reacting masses and the conditions, the β-compound being often formed in great excess. The formation of both the α and β in this fashion suggested a probable similarity to the reactions that I have found when phthalimide and phenylhydrazine interact. In fact, a complete parallelism exists between the two sets of reactions. In the case of the phthalic anhydride and the phenylhydrazine, the first phase is the addition of the two with the formation of anilidophthalamic acid:

$$C_6H_4\begin{cases}CO\\CO\end{cases}>O + NH_2NHC_6H_5 = C_6H_4\begin{cases}CONHNHC_6H_5\\COOH\end{cases}.$$

Anilidophthalamic acid is readily decomposed by heat, the decomposition taking place in two ways, with the formation of both α- and β-phthalylphenylhydrazine.

Semicarbazide hydrochloride and phthalic anhydride react readily when subjected to heat, with the formation of phthalylsemicarbazide:

$$C_6H_4\begin{cases}CO\\CO\end{cases}>O + NH_2CONHNH_2.HCl =$$

$$C_6H_4\begin{cases}CO\\CO\end{cases}>NCONHNH_2 + H_2O + HCl.$$

Phthalylsemicarbazide is readily soluble in dilute alkali, and on acidifying this solution phthalic acid monosemicarbazide precipitates:

$$C_6H_4\begin{cases}CO\\CO\end{cases}>NCONHNH_2 + KOH = C_6H_4\begin{cases}CONHCONHNH_2\\COOK\end{cases}.$$

[1] *Gazz.*, **16**, 205 (1886).
[2] *J. prakt. Chem.* [2], **35**, 270 (1887).
[3] *Gazz.*, **17**, 278 (1887).

$$C_6H_4\begin{cases}CONHCONHNH_2\\COOK\end{cases} + HCl = C_6H_4\begin{cases}CONHCONHNH_2\\COOH\end{cases}.$$

The formulae ascribed to these semicarbazide derivatives is based on the assumption that semicarbazide hydrochloride acts similarly to phenylsemicarbazide, yet the question can not be settled beyond peradventure until a thorough study has been made of their decomposition products. That the formula given to the phthalic acid monosemicarbazide is more likely to be correct than the following,

$$C_6H_4\begin{cases}CONHNHCONH_2\\COOH\end{cases},$$

is shown by the fact that a solution of this acid is not oxidized in the least even after two hours boiling with mercuric oxide. If the latter formula were correct, we should expect the formation of an azo body.

Experimental Work.

Action of phenylsemicarbazide on phthalic anhydride.

When phenylsemicarbazide and phthalic anhydride are thoroughly mixed in equimolecular proportions, and this mixture heated in a flask in an oil-bath, as the temperature rises, the mass gradually melts and at about 140-145°, the contents of the flask are completely fluid. If the bath is held at this temperature for a few minutes, and the contents of the flask stirred with a glass rod, it soon becomes pasty and then completely solidifies to a light yellow mass. This product was purified by crystallization from glacial acetic acid, from which, however, it deposits with extreme slowness in small white clusters of microscopic needles. This product is slightly soluble in alcohol and water, but is practically insoluble in all the other ordinary solvents. On heating, this substance turns yellow before fusion takes place; it melts at 191-192° with evolution of gas, the melt being of a yellow color.

On analysis, this substance proved to be phthalic acid monophenylsemicarbazide, $C_6H_4\begin{cases}CONHCONHNHC_6H_5\\COOH\end{cases}$.

	Calculated for $C_{15}H_{13}N_3O_4$.	Found.
Nitrogen	14.04	14.53

If during the preparation of this substance, after the mass has solidified, the temperature of the bath be raised, at 180-185° the mass softens and becomes a deeper yellow and finally liquefies with vigorous evolution of gas. The gas given off at first is primarily carbon dioxide containing some ammonia, but as the gas evolution proceeds, the carbon dioxide decreases in amount while the amount of ammonia increases. During the early stages of the decomposition, phenylhydrazine is plainly discernible in the escaping gases. After heating for a half hour at 180-185°, the gas evolution practically ceases and the decomposition is complete. After cooling, the contents of the flask were crystallized from alcohol. The first crop of crystals (A) was filtered and the mother-liquor concentrated. On standing, this concentrated mother-liquor deposited another crop of crystals (B). The filtrate from B, on further concentration, deposited still a third crop (C). Fractions A and B were purified by repeated crystallization from alcohol.

Fraction A crystallized from alcohol in white needle-like crystals having a melting-point of 229°. Its melting-point, crystalline form and analysis showed that the product A was phthalimide.

	Calculated for $C_8H_5O_2N$.	Found. I.	Found. II.
Carbon	65.3	65.0	...
Hydrogen	3.4	3.8	...
Nitrogen	9.5	..	9.8

Product C was likewise purified from alcohol after treating with cold alkali, filtering from the insoluble portion, and reprecipitation with acids. It deposited from alcohol in small white prisms having a melting-point of 210°. This product was identified as 1,4-diketo-2-phenyl-1,2,3,4-tetrahydro-2,3-benzdiazine. On analysis, the following results were obtained:

	Calculated for $C_{14}H_{10}O_2N_2$.	Found. I.	Found. II.	Found. III.
Carbon	70.58	70.28	...	...
Hydrogen	4.2	4.47	...	...
Nitrogen	11.76	...	12.27	12.18

Product B was only small in amount and in attempting to purify it by crystallization from glacial acetic acid, it was noticed that the product invariably separated in two forms, one lemon-yellow, the other white in color. Glacial acetic acid, while an

excellent medium from which to crystallize this substance, did not seem able to effect a separation of the two, so that the two forms were finally separated by hand, a comparatively simple task, as the crystals were of good size. The lemon-yellow crystals on analysis gave the following results:

	Calculated for $C_{14}H_{10}O_2N_2$.	Found. I.	II.	III.	IV.
Carbon	70.58	71.36	71.22	...	...
Hydrogen	4.2	4.45	4.6	...	...
Nitrogen	11.76	...	...	11.88	11.85

The white crystals gave the following results on analysis:

	Calculated for $C_{14}H_{10}O_2N_2$.	Found. I.	II.	III.
Carbon	70.58	70.30	...	...
Hydrogen	4.2	4.14	...	...
Nitrogen	11.76	...	12.26	12.16

These two sets of analyses made it evident that the substances dealt with were of the same percentage composition. The lemon-yellow substance melted at 179-179.5°, while the white body on heating in a melting-point tube, turned yellow before melting and then showed the same melting-point as the lemon-yellow substance. The analyses and the question of the melting-point showed that these two substances were either stereochemical or physical isomers. Further study of this question showed that it was a case of physical isomerism. The two substances analyzed were phthalylphenylhydrazine, $C_6H_4\begin{matrix}CO\\ \\ CO\end{matrix}>NNHC_6H_5$.

With respect to this compound, it is interesting to note that both Pickel and Hötte state that when warmed with concentrated sulphuric acid, a wine-red or violet color is produced. I have never succeeded in obtaining anything but the faintest suggestion of a violet color, just visible against the white background of an evaporating dish. However, if a trace of an oxidizing agent is added, an intense violet color is developed. That is, this compound gives the Bülow reaction with great sharpness. Doubtless both Pickel and Hötte worked with sulphuric acid containing more or less nitric acid. The reaction is very sensitive and may be used to detect nitric or other oxidizing agents in sulphuric acid. Pellizzari has noted the fact that this compound gives an intense color with nitric and sulphuric acids.

PREPARATION OF THE STABLE FORM OF $C_{14}H_{10}N_2O_2$.

The phthalylphenylhydrazine used in these experiments as well as those on the labile modification, was prepared by the methods of both Just[1] and Hötte,[2] except that the temperature was raised until the mixtures were fluid, and then held at this point until the gas evolution had ceased. The product obtained was, in both cases, ground until quite fine and then treated with dilute alkali to remove all the β-isomer present.

The following method has proved the most satisfactory in preparing considerable amounts of the yellow or stable modification: Dissolve phthalylphenylhydrazine in boiling glacial acetic acid and continue the addition of the solid until the solution is about saturated. Lower the flame under the boiling solution and allow the temperature to fall very slowly. In about an hour, the liquid will have deposited bright lemon-yellow crystals which may be readily separated from the hot mother-liquor by decantation. The crystals remaining in the flask should then be rapidly washed twice with fresh portions of glacial acetic acid and then finally dried between folds of filter-paper. Prepared in this way, the stable modification may be obtained quite free from the labile. This modification on analysis gave the following results:

	Calculated for $C_{14}H_{10}O_2N_2$.	Found.
Nitrogen.....	11.76	12.07

PREPARATION OF THE LABILE FORM OF $C_{14}H_{10}O_2N_2$.

Perhaps the simplest method for the preparation of this modification, is to heat phthalylphenylhydrazine until it becomes thoroughly fluid, and then cool rapidly. The cooled mass is usually a yellow varnish-like mass, which, on flooding with alcohol, immediately begins to crystallize in the colorless labile form. The production of the labile modification by crystallization from solvents, especially if *complete* absence of the other modification is looked for, is rather uncertain of accomplishment. Many experiments have been carried out with various solvents under different conditions of concentration, temperature, etc., but no condition was found that was absolutely certain to produce the labile form quite free from the stable every time the experiment was repeated. Microscopic examination of the colorless

[1] *Ber.*, **19**, 1204 (1886).

[2] *J. prakt. Chem.* [2], **35**, 268 (1887).

Fig. I.

form almost invariably showed traces of the yellow modification. Reference should be made to two cases which frequently gave excellent results, *i. e.*, produced the white modification with but very small amounts of the other. In one case, a quite concentrated and hot glacial acetic acid solution of phthalylphenylhydrazine was placed in boiling-hot water in a beaker which was thoroughly insulated with hair felt, in consequence of which the temperature of the solvent dropped quite slowly. In this case, the labile modification separated practically free from the yellow, except at the bottom of the tube in which the crystallization took place. Again, the white modification has been obtained frequently from an alcoholic solution, especially when the solution had stood quietly and had reached room temperature before crystallization took place. It must, however, be borne in mind, that absolute certainty as to the results are not to be expected from these two methods. A sample of the white modification prepared by the use of glacial acetic acid as a solvent, gave the following results on analysis:

	Calculated for $C_{14}H_{10}O_2N_2$.	Found.
Nitrogen.....	11.76	12.09

Ordinarily, from such solvents as glacial acetic acid, benzene, alcohol, acetone, etc., both forms appear together. Solutions of both the white and yellow modifications are yellow.

The above figure shows both forms together. The magnification is twenty-five diameters. This preparation was made by heating phthalylphenylhydrazine on a microscope slide until the solid had become quite liquid. By means of a warm platinum spatula, the fluid was spread out over the slide in a thin layer, and then immediately dropped on the surface of a mercury bath in order to cool the slide rapidly. When cold, the slide was found covered with a thin layer of a yellow varnish-like mass, which, on flooding with alcohol, immediately began to separate the white modification in the form of minute crystals. The slide was then carefully heated at one point in order to convert the white into the yellow form. With care, this conversion may be accomplished without fusing the labile form. In the above figure, the feathery fringe of crystals are the white, while the heavier and more compact masses are the yellow modification. Under the microscope, the distinction in color between these two is most marked.

The transition temperature of the labile into the stable form was not determined, although it was observed that five hours' heating in a Victor Meyer bath at 95° did not effect any change, but at 150°, the conversion is complete in a very few minutes. In the latter case, the temperature of the bath was controlled by boiling anisol (b. p. 155°).

The best method for obtaining both these forms in characteristic crystals, is to crystallize slowly from hot acetone. When such a solution is placed in a shallow layer in a crystallizing dish and allowed to cool spontaneously, it frequently is a matter of many hours before crystallization takes place. Both forms usually occur together, but the crystals are of such a size that they may be readily separated by hand. I am indebted to Professor E. H. Kraus of this University for the following observations as to the crystallographic development of these modifications, the crystals measured being obtained from acetone.

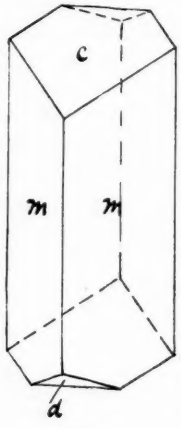


Fig. 2.

YELLOW MODIFICATION.

The crystals of this modification (Fig. 2) were clear, transparent, distinctly yellow in color, and about 2 to 5 mm. in length. The usual combination, as shown by Fig. 2, consists of the unit prism, $m\ \{110\}$, the basal pinacoid, $c\ \{001\}$, and the positive hemiorthodome, $d\ \{\bar{1}01\}$. The habitus is generally prismatic in that the unit prism predominates. The measurements are as follows:

CRYSTAL SYSTEM: MONOCLINIC, HOLOHEDRAL.

$a:b:c = 1.1671:1:0.7848.$

$\beta = 54° 50'.$

	Observed.	Calculated.
$110 : 1\bar{1}0 =$	87° 18′	.....
$\bar{1}10 . \bar{1}01 =$	85° 8′	. ....
$110 : 001 =$	65° 22′	.....
$001 : \bar{1}01 =$	42° 6′	41° 54′

A very perfect cleavage parallel to the faces of the unit prism, $m\ \{110\}$, was noted.

WHITE MODIFICATION.

These crystals are colorless and transparent, and usually 2 to 3 mm. in length and about 1 mm. in thickness. Fig. 3 shows the

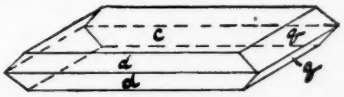


Fig. 3.

usual combination of forms and consists of the basal pinacoid, $c\ \{001\}$, the macrodome, $d\ \{101\}$, and the brachydome, $q\ \{011\}$. The basal pinacoid usually predominates, which gives the crystals a tabular habitus. Inasmuch as most of these forms give quite good signals, the measurements are, for the most part, to be considered as accurate. The measurements are as follows:

CRYSTAL SYSTEM: ORTHORHOMBIC, HOLOHEDRAL.

$a:b:c = 0.2526:1:0.9118.$

	Observed.	Calculated.
001 : 011 =	42° 21½′	.....
001 : 101 =	74° 31′	.....
101 : 011 =	78° 38′	78° 43′

A perfect cleavage parallel to the basal pinacoid, $c\ \{001\}$, was noted.

THE ACTION OF PHENYLHYDRAZINE ON PHTHALIMIDE.

Equimolecular quantities of phthalimide and phenylhydrazine were heated together in a flask immersed in an oil-bath, the temperature of the bath being gradually raised until it registered 120°. During this operation, the mixture was constantly stirred with a glass rod. As the temperature increased, the mass assumed a yellow color and ammonia was given off. In a few minutes the mass solidified. It was then ground fine and washed with cold alcohol, a pure white product being obtained by this treatment. After being crystallized from alcohol, the substance was submitted to analysis with the following results:

	Calculated for $C_{14}H_{10}N_2O_2$.	Found.		
		I.	II.	III.
Nitrogen.....	16.47	17.52	17.58	17.34

While the analyses are not as close as could be wished for, yet they show that the substance is anilidophthaldiamide. This substance is so readily decomposed that although numerous

methods of purification were tried, none gave any better results than simple crystallization from alcohol, the hot alcoholic solution, however, being rapidly cooled in ice water. Hötte[1] also obtained this compound during the course of his work, and likewise found it sufficiently unstable and difficult of purification, so that accurate analytical figures were not obtainable. The method of preparation used by Hötte in making this substance, was that of treating phthalylphenylhydrazine with alcoholic ammonia. He gives its melting-point as 146°, but I was unable to obtain a satisfactory melting-point as the substance decomposes so readily, figures being obtained from 156-185°, but none of them so low as that given by Hötte. Melting was always accompanied by evolution of gas and the conversion of the compound into a yellow substance.

It is worthy of notice that even during the solution of the anilidophthaldiamide in alcohol with the aid of heat, decomposition takes place to such an extent that it is comparatively easy to show the presence of both α- and β-phthalylphenylhydrazine in the solution.

Anilidophthaldiamide crystallizes from alcohol in very small colorless flat prisms. This substance is soluble in hot acetone and glacial acetic acid, but less soluble in ethyl acetate. In all other of the ordinary solvents, this compound is practically insoluble.

The ease with which phenylhydrazine and phthalimide combine is seen by the fact that if they are mixed in equimolecular proportions and allowed to stand at ordinary temperatures, in a few hours the odor of ammonia is easily detected, and, in a day or two, the mixture has set to a dense solid mass of anilidophthaldiamide,

DECOMPOSITION OF ANILIDOPHTHALDIAMIDE BY HEAT.

In carrying out this work, experiments have been made with the purest anilidophthaldiamide I have been able to prepare, as well as with the crude product without purification. The results were the same in both cases. If phenylhydrazine and phthalimide are heated together to 120° and stirred until the mass becomes solid, the resultant crude anilidophthaldiamide may be readily decomposed by carrying the temperature still higher. If the temperature of the bath in which the mass is being heated is carried up to 140°, the solid mass again liquefies and ammonia is evolved

[1] *J. prakt. Chem.* [2], **35**, 280 (1887).

in great quantities. Fifteen minutes is usually a sufficient length of time to heat the mixture in order to bring the decomposition to an end. The resultant product was crystallized from alcohol, the product which separated being practically pure α-phthalylphenylhydrazine, as was easily shown by the melting-point, and presence in the two isomeric forms. The filtrate from this crop of crystals was evaporated to a very small bulk, and, after standing for some time, the crystals which separated were thoroughly ground and treated with dilute alkali. The alkaline solution, after acidifying, deposited a white precipitate which was filtered off and crystallized from alcohol. This product had the melting-point of 210° and was readily identified as β-phthalylphenylhydrazine. The portion insoluble in the dilute alkali was the α isomer.

THE ACTION OF PHENYLHYDRAZINE ON PHTHALIC ANHYDRIDE.

Equimolecular quantities of these two substances were dissolved separately in chloroform and the solutions then mixed. The mixture became warm and shortly began to separate a white crystalline product. After standing for several hours, this was filtered and washed with a little chloroform. After crystallization from alcohol, this substance gave the following results:

	Calculated for $C_{14}H_{12}O_3N_2$.	Found.
Nitrogen.....	10.93	10.90

The above analysis identified the body as anilidophthalamic acid.

The yield was about 65 per cent. of the theory and the acid was practically pure without crystallization from alcohol. It is rather easily decomposed, an alcoholic solution of it darkening slowly when boiled. The melting-point was uncertain and could not be satisfactorily determined on account of the ease with which the acid decomposes. Hötte gives it as 165-166° and Pellizzari as 163°, but while attempts have been made many times to get satisfactory duplicate melting-points, yet I have been unable to obtain them. This method for the preparation of this addition product is greatly superior to the method of Hötte, being very much more rapid and the product much purer.

DECOMPOSITION OF ANILIDOPHTHALAMIC ACID BY HEAT.

The pure acid was heated until fused and the gas evolution which took place on melting had ceased. The resulting product

was treated exactly as described above with respect to the product obtained by heating anilidophthaldiamide. Furthermore, the decomposition products isolated were the same, namely, both α- and β-phthalylphenylhydrazine.

In the decomposition of the anilidophthalamic acid, the relative proportions of the α- and β-bodies formed, depends on the temperature at which the decomposition takes place. Two experiments will show this clearly:

(1) The acid was placed in a small Erlenmeyer flask and heated in an oil-bath until the bath registered 160-170°. In a few minutes the mass had completely liquefied and the gas evolution had ceased. The decomposition product was removed from the flask and the β-isomer separated from the α by its solubility in alkali. The result showed that the decomposition product was composed of 20 per cent. of the β and 80 per cent. of the α.

(2) A flask was heated in an oil-bath until the bath registered 210°. The acid was introduced then in small portions, each portion having completely melted and the gas evolution ceased before a fresh lot of acid was added. The decomposition product was separated into its constituents as in the previous experiment, and it was found that there had been formed 40 per cent. of the β-isomer and 60 per cent. of the α isomer.

ACTION OF SEMICARBAZIDE HYDROCHLORIDE ON PHTHALIC ANHYDRIDE.

When equimolecular quantities of semicarbazide hydrochloride and phthalic anhydride are intimately mixed and heated in a flask in an oil-bath, when the bath registers about 150°, the mixture is a soft and pasty mass. At 160°, hydrochloric acid is freely evolved. The temperature was held at 160° for one hour, at the expiration of which time, the hydrochloric acid had practically ceased being evolved. Occasionally, the mass will solidify at this elevated temperature when stirred with a glass rod. The cooled mass was then crystallized from glacial acetic acid, from which it separates in white needles. The pure product is slightly soluble in boiling water and alcohol, but insoluble in the other solvents. It melts at about 262° with gas evolution, the melt being yellow. On analysis, the following results were obtained:

	Calculated for $C_9H_7O_3N_3$.	Found.		
		I.	II.	III.
Nitrogen.....	20.48	20.47	20.35	20.75

Phthalylsemicarbazide dissolves readily in cold alkalies, momentarily turning yellow. When this solution is acidified, a white crystalline precipitate is obtained, which is readily purified by crystallization from water, in which it is readily soluble and from which it separates in slender, white prisms. This product is soluble in alcohol and glacial acetic acid, but insoluble in ether, chloroform and benzene.

This substance, like phthalylsemicarbazide, melts at about 262°, with gas evolution, the melt being yellow. That this phthalic acid monsemicarbazide has the same melting-point as the phthalylsemicarbazide, is due to the fact that the former is converted into the latter before fusion takes place.

On analysis, the following results were obtained:

	Calculated for $C_9H_9O_4N_3$.	Found. I.	Found. II.
Carbon	48.43	48.72	...
Hydrogen	4.04	4.28	...
Nitrogen	18.83	...	18.84

CHEMICAL LABORATORY, UNIVERSITY OF MICHIGAN,
July 1, 1905.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE NEBRASKA WESLEYAN UNIVERSITY.]

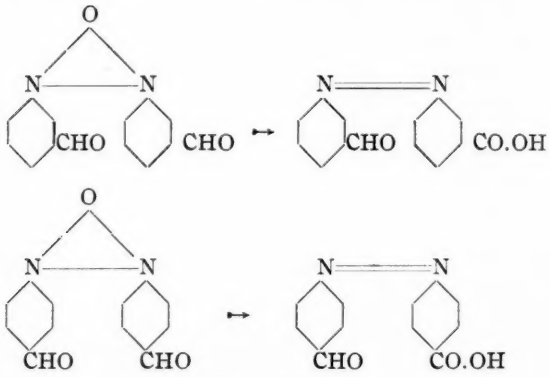
THE BENZALDEHYDE-AZO-BENZOIC ACIDS.

BY FREDERICK J. ALWAY AND WALTER D. BONNER.

Received July 5, 1905.

THE ISOMERIC *m*- and *p*-azoxybenzaldehydes and many of their derivatives were described by one of us[1] three years ago, it being stated[2] at the time that when *p*-azoxybenzaldehyde is heated with concentrated sulphuric acid to 110° to 120° it is changed into a brown substance, which shows the characteristic properties of the oxyazo compounds. Since then Human and Weil[3] in several publications have contended that, instead of the change indicated above taking place, the two azoxybenzaldehydes when heated with concentrated sulphuric acid, pass into the isomeric benzaldehydeazobenzoic acids, as represented by the following equations:

[1] *Am. Chem. J.*, **28**, 34, 475.
[2] *Ibid.*, **28**, 476.
[3] *Ber.*, **36**, 3469, 3801; Human: Inaugural Dissertation, Univ. of Basel, 1904.



As is well known, the change of the poorly characterized azoxy compounds into the highly colored oxyazo compounds, whose salts act as powerful dyes, has long been used as a means of deciding whether newly discovered compounds contain the azoxy group. "The most interesting reaction of the azoxy compounds is the change into oxyazo compounds, which many of them undergo when gently warmed with concentrated sulphuric acid."[1] The reaction, indicated above, appeared remarkable not only in that it was new to the azoxy compounds, but also in that it was the first instance in which an oxygen atom attached to a nitrogen atom had been found to pass to a carbon atom in the meta position. Moreover, in this case, both the para and the ortho positions were free for the oxygen atom to enter. Human and Weil recognized the unusual character of the reaction but believed that the presence of one carboxyl group and of only one aldehyde group in the molecule was fully established by the following:

(1) The meta compound forms a sodium salt, $C_{14}H_9O_3N_2Na$. They observed, however, that this salt, when brought into contact with pure water, dissociated, setting free the compound $C_{14}H_{10}O_3N_2$.

(2) By treating the meta compound $C_{14}H_{10}O_3N_2$, melting at 163°, with alcohol and hydrochloric acid, according to the method of Victor Meyer, they obtained a substance melting at 156° and not entirely dissolved by sodium carbonate solution. The single analysis of the compound made, a nitrogen determination, sup-

[1] Meyer u. Jacobson: *Lehrb. organ. Chem.*, **2**, Part I, 251.

ported the idea that this substance was the ethyl ester of *m*-benzaldehydeazobenzoic acid.

(3) They obtained condensation products of the meta compound with one molecule each of aniline, hydroxylamine, hydrazine and phenylhydrazinesulphonic acid, according to the equation:

$$C_{13}H_9O_2N_2.CHO + H_2N.X = C_{13}H_9O_2N_2.CH = N.X + H_2O,$$

where X represents the groups $—C_6H_5$, —OH, $—NH_2$, and $—NH.C_6H_4.SO_3H$. Their conclusions in regard to the para compound seem to have been based upon analogy rather than upon experimental data, as while they describe *p*-benzaldehydeazobenzoic acid as a reddish brown powder, melting above the boiling-point of sulphuric acid, and its ethyl ester as melting at 60°, they report no analyses of the para compound or of its derivatives.

As the result of our investigations we conclude that *m*-azoxybenzaldehyde, when heated with concentrated sulphuric acid, changes to the isomeric oxyazobenzaldehyde, the position of the oxy group in the latter not having been determined, and that *p*-azoxybenzaldehyde by similar treatment is changed into several oxyazo compounds of unknown constitution. That the compound obtained by Human and Weil is not *m*-benzaldehydeazobenzoic acid is evident from the fact that we obtained *m*-benzaldehydeazobenzoic acid synthetically, condensing *m*-nitrosobenzaldehyde with *m*-amidobenzoic acid, and by saponifying its ethyl ester, which itself was prepared by the condensation of *m*-nitrosobenzaldehyde with the ethyl ester of *m*-amidobenzoic acid. The acid melts at 230° and the ethyl ester at 90°. The acid condenses with a single molecule of phenylhydrazine to form a hydrazone. Its salts are stable in contact with water and do not stain the skin or dye silk or wool. The synthesis of the acid and its ester according to the equations

$$OHC.C_6H_4.NO + H_2N.C_6H_4.COOH = OHC.C_6H_4.N = N.C_6H_4.COOH + H_2O$$

and

$$OHC.C_6H_4.NO + H_2N.C_6H_4.COOC_2H_5 = OHC.C_6H_4.N = N.C_6H_4.COOC_2H_5 + H_2O$$

leaves no doubt as to their being the compounds to which the formulas of *m*-benzaldehydeazobenzoic acid and its ester should be assigned. The compound of acid nature obtained by Human and Weil melts at 163° and its supposed ester at 156°. Its salts

are unstable in contact with water, stain the skin and dye silk and wool orange. These properties are characteristic of oxyazo compounds and not of carboxyl derivatives of azobenzene, the latter not acting as dyes. "Carboxyl derivatives of azobenzene possess scarcely any dying properties."[1] Repeated attempts to esterify the compound failed, the unchanged original substance remaining. The assumption of Human and Weil that, after the attempted esterification, the portion that does not dissolve in sodium carbonate solution is an ester, is not justified, because the compound melting at 163° is, itself, only sparingly soluble in cold sodium carbonate. The presence of two aldehyde groups in the molecule is apparent from the formation of condensation products with two molecules each of aniline, hydroxylamine and phenylhydrazine when these three compounds were used in excess under favorable conditions.

$$C_{14}H_{10}O_3N_2 + 2H_2N.C_6H_5 + C_{14}H_{10}ON_2.(N.C_6H_5)_2 + 2H_2O$$

$$C_{14}H_{10}O_3N_2 + 2H_2N.OH + C_{14}H_{10}ON_2.(N.OH)_2 + 2H_2O$$

$$C_{14}H_{10}O_3N_2 + 2H_2N.NH.C_6H_5 = C_{14}H_{10}ON_2.(N.NH.C_6H_5)_2 + 2H_2O$$

The dianilide, $C_{14}H_{10}ON_2.(N.C_6H_5)_2$, when treated with aqueous alcohol, splits off one molecule of aniline and forms the monoanilide described by Human and Weil.

p-Benzaldehydeazobenzoic acid was obtained by the condensation of both *p*-nitrosobenzaldehyde with *p*-amidobenzoic acid and *p*-amidobenzaldehyde with *p*-nitrosobenzoic acid:

$$OHC.C_6H_4.NO + H_2N.C_6H_4.COOH = OHC.C_6H_4.N=N.C_6H_4.COOH + H_2O.$$

$$OHC.C_6H_4.NH_2 + ON.C_6H_4.COOH = OHC.C_6H_4.N=N.C_6H_4.COOH + H_2O.$$

The ethyl ester of *p*-benzaldehydeazobenzoic acid was prepared by the condensation of *p*-nitrosobenzaldehyde with the ethyl ester of *p*-amidobenzoic acid, and by the analogous condensation of *p*-amidobenzaldehyde with the ethyl ester of *p*-nitrosobenzoic acid:

$$OHC.C_6H_4.NO + H_2N.C_6H_4.COOC_2H_5 = OHC.C_6H_4.N=N.C_6H_4.COOC_2H_5 + H_2O.$$

$$OHC.C_6H_4.NH_2 + ON.C_6H_4.COOC_2H_5 = OHC.C_6H_4.N=N.C_6H_4.COOC_2H_5 + H_2O.$$

[1] *Lehrb. organ. Chem.*, **2**, Part 1, p. 270.

The acid is infusible below the boiling-point of sulphuric acid, while the ester melts at 159°. The salts of the acid are stable and do not act as dyes. The substance obtained by heating *p*-azoxybenzaldehyde with concentrated sulphuric acid forms unstable salts which act as powerful dyes. We were unable to esterify it, although Human and Weil claim to have obtained the ester, melting at 60°. The transposition product of *p*-azoxybenzaldehyde is clearly not *p*-benzaldehydeazobenzoic acid. It is evidently a mixture of several oxyazo compounds, none of which we were able to isolate.

p-Nitrosobenzaldehyde condenses also with two molecules of the ethyl ester of *p*-amidobenzoic acid, according to the equation

$$C_2H_5.OOC.C_6H_4.NH_2 + OHC.C_6H_4NO + H_2N.C_6H_4.COOC_2H_5 = C_2H_5.OOC.C_6H_4.N=HC.C_6H_4.N=N.C_6H_4COOC_2H_5 + H_2O.$$

This compound when treated with dilute acids readily splits off one molecule of the ethyl ester of *p*-amidobenzoic acid, forming the ethyl ester of *p*-benzaldehydeazobenzoic acid.

p-Azobenzaldehyde was obtained by the condensation of *p*-amidobenzaldehyde with *p*-nitrosobenzaldehyde:

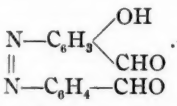
$$OHC.C_6H_4.NH_2 + ON.C_6H_4.CHO = OHC.C_6H_4.N=N.C_6H_4.CHO + H_2O.$$

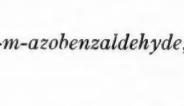
It had previously been prepared by Freundler[1] by the action of dilute sulphuric acid upon the acetal $(CH_3O)_2CH.C_6H_4.N=N.C_6H_4.CH.(O.CH_3)_2$, which was obtained by the alkaline reduction of the dimethylacetal of *p*-nitrobenzaldehyde.

EXPERIMENTAL PART.

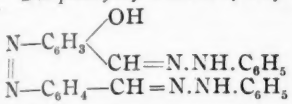
Preparation of m-Azoxybenzaldehyde.—Fifteen grams of *m*-nitrobenzaldehyde were dissolved in 2 liters of boiling water and treated with 60 grams of ferrous sulphate; this mixture was heated a short time and then poured gradually, with constant stirring, into 150 cc. of 15 per cent. solution of sodium hydroxide. After the mixture had been allowed to stand, with frequent stirring, half an hour, we added, instead of the bisulphite used by Human and Weil, 120 cc. of concentrated hydrochloric acid, then warmed and stirred until the iron compounds, that had been precipitated, were dissolved. The *m*-azoxybenzaldehyde was filtered out, thoroughly washed with water and dried. The yield was 12 grams, Human and Weil having obtained only 8 grams by the bisulphite method.

[1] *C. R.*, **134**, 1359.

Oxy-m-azobenzaldehyde,  .—In the preparation of this compound we followed the method described by Human and Weil for the preparation of what they considered *m*-benzaldehydeazobenzoic acid. Five grams of *m*-azoxybenzaldehyde were placed in a flask with 25 grams of concentrated sulphuric acid, a yellow solution being formed, which was heated in an oil-bath for two hours, the temperature being kept at 110° by means of a thermoregulator. At the end of this time the solution, which had changed in color to a dark red, was poured into ice water, a yellow solid being precipitated. This substance, melting at 160° (uncorr.), (Human and Weil give 161°), is only slightly soluble in a cold solution of sodium carbonate. A specimen, melting at 165° (cor.), that had been purified by dissolving the crude substance in hot sodium carbonate solution and precipitating by means of a dilute acid, was ground in a mortar with a cold saturated solution of sodium carbonate. Very little gas was evolved and after grinding twenty minutes very little of the substance had gone into solution. The contents of the mortar were then transferred to a test-tube and heated, the solid being gradually dissolved with a vigorous evolution of gas, while the color changed first to brown and finally to deep red. This oxyazobenzaldehyde dissolves to a slight extent in cold solutions of alkaline carbonates and in dilute solutions of ammonia and the alkaline hydroxides, with a yellow to orange color. In concentrated solutions of the alkaline hydroxides or of ammonia and in hot solutions of the alkaline carbonates it is readily soluble, forming brown to deep red solutions. These solutions stain the skin and dye silk and wool an orange-yellow.

The Sodium Salt of Oxy-m-azobenzaldehyde,  .—This salt was obtained by cooling the saturated solution of oxy-*m*-azobenzaldehyde, prepared by boiling the latter with a saturated solution of sodium carbonate. It forms very small, brick-red crystals that do not melt below the boiling-point of sulphuric acid.

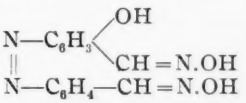
Bis-phenylhydrazone of Oxy-m-azobenzaldehyde,



.—An alcoholic solution of oxy-*m*-azobenzaldehyde was heated one hour on the water-bath with an excess of phenylhydrazine. On cooling the solution light brown crystals, melting at 234° (corr.), separated out.

	Calculated for $C_{26}H_{22}O_{2}N_{6}$.	Found.
Nitrogen.....	19.4	19.3

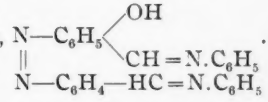
Dioxime of Oxy-m-azobenzaldehyde,



.—A solution of 0.8 gram of sodium hydroxide in water was treated with 0.5 gram of hydroxylamine hydrochloride and 0.6 gram of the sodium salt of the oxy-*m*-azobenzaldehyde and the whole heated an hour and a half on the water-bath. The red solution, so obtained, when filtered and acidified with dilute acetic acid gave a yellow gelatinous precipitate, which was filtered out, dried on a porous plate and recrystallized from dilute alcohol. The dioxime forms brownish yellow crystals, melting at 207° to 211° (cor.).

	Calculated for $C_{14}H_{12}O_{3}N_{4}$.	Found.
Nitrogen.....	19.7	19.8

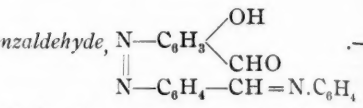
Dianilide of Oxy-m-azobenzaldehyde,



.—Two grams of oxy-*m*-azobenzaldehyde were treated with 5 cc. of freshly distilled aniline. The mixture rose rapidly in temperature and assumed a red color. After it had been heated half an hour at 110°, the clear solution solidified, when cooled and stirred. The dark colored solid was dried on a porous plate, dissolved in boiling benzene and precipitated by the gradual addition of absolute alcohol.

The compound forms bright yellow crystals, melting at 141° (corr.).

	Calculated for $C_{26}H_{20}ON_{4}$.	Found.
Nitrogen.....	13.8	13.8

Monanilide of Oxy-m-azobenzaldehyde,  .—

This compound was prepared in the same way as the dianilide, with the exception that the benzene solution was treated with 95 per cent. alcohol instead of absolute alcohol. It forms small yellow crystals, melting at 126° to 130°.

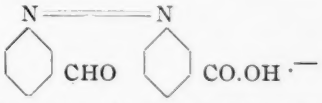
	Calculated for $C_{20}H_{15}O_2N_3$.	Found.
Nitrogen.....	12.8	12.9

This anilide was prepared also by the method of Human and Weil, who give the melting-point as 128°. The sodium salt of oxy-*m*-azobenzaldehyde was heated with an aqueous solution of sodium hydroxide and aniline. The crude anilide, recrystallized from 95 per cent. alcohol, was similar in properties to that described above.

Two specimens of monanilide, one from each method of preparation, were boiled with dilute hydrochloric acid. The yellow residues were well washed with water and dried. Both melted at 165°, the melting-point of the oxy-*m*-azobenzaldehyde.

The Action of Oxy-m-azobenzaldehyde with Alcohol and Hydrochloric Acid.—We made repeated attempts to obtain the ester, following the method described by Human and Weil. The phenomena were the same in each case and similar to those observed by these investigators. Two grams of oxy-*m*-azobenzaldehyde and 20 cc. of 95 per cent. alcohol were placed in a strong bottle. Dry hydrochloric acid gas was led into the mixture, which was kept cool by means of salt and ice, until an increase in weight of 6 grams had taken place. As the hydrochloric acid was introduced the color of the mixture changed to red and finally blood-red. The bottle was then stoppered tightly and allowed to stand twenty-four hours. It was then connected with a return-condenser and heated one hour on the water-bath. The reaction mixture was filtered and the filtrate evaporated to half its volume, a considerable amount of red solid separating out during the latter operation. Water was added to complete precipitation and the yellowish brown precipitate filtered out and treated with cold sodium carbonate solution. Part of it dissolved and the residue, which, when washed with water and dried, melted at 150° to 160°, was almost entirely soluble in hot sodium carbonate solution or in a

large quantity of cold sodium carbonate solution. The very small amount of substance that did not dissolve in sodium carbonate solution did not melt below 200°. The quantity of it was too minute for further investigation. When the mixture of oxyazobenzaldehyde, alcohol and hydrochloric acid was allowed to stand forty-eight hours the results were the same. In one case after adding the 6 grams of hydrochloric acid some of the red solution was poured into water. A yellow precipitate, melting at 155° to 159° and forming an anilide melting at 126°, was obtained. After the bottle had stood twenty-four hours the contents were filtered out. Blood-red crystals were obtained. On standing exposed to the air these lost hydrochloric acid and formed a brownish yellow solid, melting at 160° and yielding an anilide melting at 126°. Oxy-*m*-azobenzaldehyde, when exposed to a current of hydrochloric acid gas, became red. Evidently the oxyazoaldehyde forms an addition-product with hydrochloric acid. Human and Weil give 156° as the melting-point of their supposed ester.

m-Benzaldehydeazobenzoic Acid, 

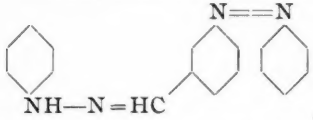
A solution of 1 gram of *m*-amidobenzoic acid in hot glacial acetic acid was added to a boiling solution of 1 gram of *m*-nitrosobenzaldehyde in glacial acetic acid. The color changed gradually from the deep green of the nitroso compound, to a dark green, then to a dark brown and finally to a black. The mixture was boiled a few minutes and then allowed to cool slowly. A light brown amorphous solid separated out. This was insoluble in ordinary organic solvents and decomposed, without melting, at 275°. It was dissolved in sodium carbonate solution, from which, on standing, a yellow solid, not melting below the boiling-point of sulphuric acid, separated out. This yellow substance, evidently the sodium salt, was dissolved in water and treated with hydrochloric acid. The crude substance, so obtained, melted at 222°. By recrystallization from acetic acid it was obtained in the form of small yellow to brownish yellow needles, melting at 230° (corr.).

	Calculated for $C_{14}H_{10}O_3N_2$.	Found.
Carbon	66.1	66.2
Hydrogen	3.9	3.7
Nitrogen	11.0	10.9

The acid was also easily obtained in pure form by warming its ethyl ester, described below, with concentrated hydrochloric acid, filtering and washing the residue with water, and finally recrystallizing from acetic acid.

The insoluble compound, first obtained from the interaction of *m*-nitrosobenzaldehyde and *m*-amidobenzoic acid is probably the condensation product, $HO_2C.C_6H_4.N:HC.C_6H_4.N:N.C_6H_4.COOH$, analogous to the para compound, melting at 152°, which is described below.

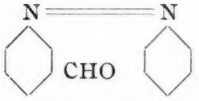
Phenylhydrazone of m-Benzaldehydeazobenzoic Acid,



—A solution of *m*-benzaldehydeazobenzoic acid in hot glacial acetic acid was treated with an excess of phenylhydrazine. The solution, on cooling, deposited orange-yellow crystals, melting at 195° (corr.).

	Calculated for $C_{20}H_{16}O_2N_4$.	Found.
Nitrogen..	16.3	16.6

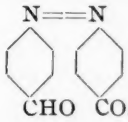
Ethyl Ester of m-Benzaldehydeazobenzoic Acid,



—A solution of 2 grams of *m*-nitrosobenzaldehyde in boiling glacial acetic acid was added to a similar solution of 2.5 grams of the ethyl ester of *m*-amidobenzoic acid. The mixture was boiled a few minutes, allowed to cool and then again heated to boiling. Water was added until a distinct turbidity was produced. On cooling, this solution deposited crystals, which were recrystallized from 80 per cent. alcohol. The latter is a satisfactory solvent for the purification of the compound, although it is usually necessary to agitate or to seed the cool solution, in order to start crystallization.

The ester forms reddish yellow needles, melting at 90° (corr.), and very soluble in alcohol, benzene and glacial acetic acid.

	Calculated for $C_{16}H_{14}O_3N_2$.	Found.
Nitrogen	9.9	10.2

p-Benzaldehydeazobenzoic Acid,  .—Molecular

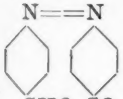
proportions of *p*-amidobenzoic acid and of *p*-nitrosobenzaldehyde were dissolved in separate portions of boiling glacial acetic acid. The solution of the former was poured into that of the latter. The color of the solution changed from green to dark brown and then, suddenly, a heavy yellow precipitate separated out, the solution changing to a solid mass. This was boiled, first with alcohol and then with glacial acetic acid to remove any unchanged amido acid or nitrosoaldehyde. The residue, when dried, formed an amorphous reddish yellow solid, insoluble in ordinary organic solvents and not melting below 300°.

	Calculated for $C_{14}H_{10}O_3N_2$.	Found.
Nitrogen.....	11.0	10.9

The same compound was obtained by the similar condensation of *p*-amidobenzaldehyde with *p*-nitrosobenzoic acid. As both of these compounds readily pass into insoluble modifications, a freshly prepared alcoholic solution of *p*-nitrosobenzoic acid was poured into an alcohol solution of freshly prepared *p*-amidobenzaldehyde. The mixture was heated to boiling, treated with three times its volume of glacial acetic acid and again heated to boiling. From this point on the method of procedure was the same as that just described.

Alkaline solutions of the acid are light yellow in color and neither dye silk and wool nor stain the skin. The solution of the acid in ammonia is quite stable and on evaporation deposits the ammonium salt, soluble in water.

Ethyl Ester of p-Benzaldehydeazobenzoic Acid,



.—A solution of *p*-nitrosobenzaldehyde (1 mol.) in boiling glacial acetic acid was slowly added to a simliar solution of the ethyl ester of *p*-amidobenzoic acid (1 mol.) and the mixture kept gently boiling two or three minutes, after which it was allowed

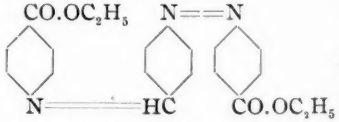
to cool slowly. At the end of twenty minutes the dark red solution began to deposit crystals and after half an hour had changed to a solid mass of red crystals. These were filtered out and recrystallized several times from glacial acetic acid.

The ester forms light red, boat-shaped crystals, melting at 159° (corr.), slighlty soluble in cold alcohol, readily soluble in hot alcohol, fairly soluble in cold glacial acetic acid and very readily soluble in the same solvent when hot.

	Calculated for $C_{16}H_{14}O_3N_2$.	Found.
Carbon	68.1	68.0
Hydrogen	5.0	4.9
Nitrogen	9.9	10.2

The compound was also obtained by the condensation of the ethyl ester of *p*-nitrosobenzoic acid with the freshly prepared soluble modification of *p*-amidobenzaldehyde. The two compounds, in molecular proportions, were dissolved in separate portions of hot absolute alcohol. When these solutions were mixed the green color of the nitroso compound persisted. Glacial acetic acid was added in excess and the whole heated to boiling, the color gradually changing to red. After standing thirty-six hours with separation of very little solid, the solution was again heated to boiling and treated with hot water until a distinct turbidity was produced. On cooling, the solution deposited a red precipitate, which, when twice recrystallized from glacial acetic acid, melted at 159° and showed the characteristic crystal form of the ester prepared by the first method.

Compound of the Formula,



—A solution of *p*-nitrosobenzaldehyde (1 mol.) in hot glacial acetic acid was poured slowly, with constant stirring, into a boiling solution of the ethyl ester of *p*-amidobenzoic acid (2 mols.). The red solution resulting from the mixture, was kept boiling a few minutes and then allowed to cool slowly. The reddish yellow crystals which separated out, were washed on the filter with alcohol, dried and recrystallized four times from benzene.

The compound forms rectangular plates, melting at 152° (corr.). The appearance of the crystals is very characteristic. Under the

microscope in transmitted light, they appear lemon-yellow. To the naked eye they appear bright red or golden yellow, according to the position of the crystals.

	Calculated for $C_{25}H_{23}O_4N_3$.	Found.
Carbon	69.8	70.1
Hydrogen	5.3	5.7
Nitrogen	9.8	9.8

The crude condensation-product, when examined under the microscope, was found to contain crystals of the ester, which melts at 159°, as well as of the compound melting at 152°. This would indicate that the condensation takes place in the two proportions, *viz.*, one molecule of nitrosoaldehyde with one molecule of the amido compound as well as one molecule of the nitrosoaldehyde with two molecules of the amido compound, even when the amido compound is present in excess.

For fuller evidence of the relation of the two condensation products, melting at 159° and 152° respectively, some of the latter was boiled with concentrated hydrochloric acid. The compound, melting at 159°, was obtained. Some of the latter compound (1 mol.), prepared by the first method, was dissolved in hot glacial acetic acid and treated with a similar solution of the ethyl ester of *p*-amidobenzoic acid (1 mol.). By cooling the mixture and recrystallizing the product from benzene, crystals were obtained which melted at 152° and possessed the characteristic appearance mentioned above.

p-Azobenzaldehyde, $OHC.C_6H_4.N:N.C_6H_4.CHO$.—Solutions in absolute alcohol of *p*-nitrosobenzaldehyde and of *p*-amidobenzaldehyde in molecular proportions, were mixed and then treated with glacial acetic acid. After the mixture had been boiled a few minutes and allowed to stand several hours it was subjected to distillation with steam until the distillate was colorless, in order to remove all unchanged nitrosobenzaldehyde. The dark-colored solid, remaining in the distilling-flask, when recrystallized from nitrobenzene formed long red needles, melting at 239° (corr.). When glacial acetic acid was used as the solvent the substance was obtained in the form of very lustrous orange-red crystals, melting at the same temperature. Freundler used nitrobenzene as solvent and found the melting-point 237° to 238°.

Action of Concentrated Sulphuric Acid upon p-Azoxybenzaldehyde.—Five grams of *p*-azoxybenzaldehyde were placed in a

flask with 25 grams of concentrated sulphuric acid and heated on an oil-bath to 110° for two hours. A slight evolution of gas was observed and the odor of sulphur dioxide was distinctly noticeable at the mouth of the flask. The dark red solution when poured into ice water gave a brown amorphous solid. This was sparingly soluble in cold sodium carbonate solution and readily soluble in hot sodium carbonate solution and in concentrated ammonia solution. It was reprecipitated from both by the addition of mineral acids. The ammonia solution when evaporated on the water-bath or allowed to evaporate at the temperature of the room deposited a red solid which was insoluble in water, but soluble in ammonia and alkalies. When heated with caustic alkalies it did not evolve ammonia. Its alkaline solutions stained the skin and dyed silk and wool orange-yellow. We did not succeed in isolating any compound in a pure condition from the crude transposition product, judging from the analytical data. As the product is insoluble in ordinary solvents and does not melt below 300° its purification is very difficult.

UNIVERSITY PLACE, NEB.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

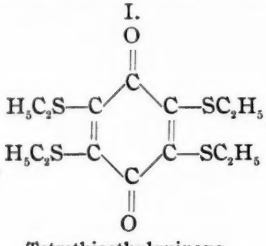
THE ACTION OF MERCAPTIDES ON QUINONES.

BY JOHN LANGLEY SAMMIS.

Received July 14, 1905.

IN A previous paper by Professor H. S. Grindley and the writer upon this subject[1], it was concluded that the reaction of sodium mercaptide on dichlordiphenoxyquinone in dry ether consisted of *substitutions* and of *addition* and, at that time, three substances resulting from this reaction were given the following formulas:

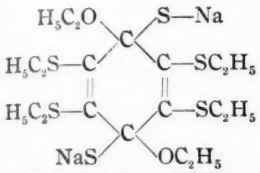
I.



Tetrathioethylquinone.

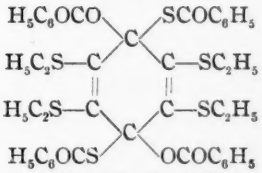
[1] *Am. Chem. J.*, 19, 293 (1897).

II.



Addition-product of sodium mercaptide and tetrathioethylquinone.

III.



Tetrathioethylquinonedibenzoyldithiobenzoylacetal.

Tetrathioethylquinone, I, was made from sodium mercaptide and dichlordiphenoxyquinone, by substitution; and also from chloranil in larger quantity, though this latter substance was not mentioned at that time. Substance II was not isolated or analyzed, but was supposed to be formed by addition when two molecules of sodium mercaptide were mixed with one molecule of tetrathioethylquinone in dry ether, or by substitution and addition when six molecules of sodium mercaptide were mixed with one molecule of chloranil or of dichlordiphenoxyquinone. Substance III was made by adding four molecules of benzoyl chloride to substance II, prepared in any of these ways. Substances II and III were considered to be somewhat analogous to the hemiacetal derivatives described by Jackson and Grindley.[1] The fact was observed by the authors of the paper referred to (but not mentioned at that time) that if substance III was prepared from chloranil, sodium mercaptide, and benzoyl chloride, then another substance was simultaneously formed, which, after recrystallizing from alcohol, proved to be the dibenzoate of tetrachlorhydroquinone described by Levy and Schulz.[2] It is clear that the formation of this latter substance involves no addition, but consists of reduction of the chloranil to tetrachlorhydroquinone, which in alkaline solution reacts with benzoyl chloride, forming the dibenzoate. In view of this, it appeared to the writer to be desirable to search for additional facts to aid in determining whether the action of mercaptides on quinones consists in general of *addition* or of *reduction* or of both.

In the course of this work, the method of making tetrathioethylquinone (Formula I above) was improved so that 95 per cent. of the theoretical yield can now be obtained, instead of 10 per cent. or less by the former methods. It was found that in the

[1] *Am. Chem. J.*, **17**, 577 (1895).
[2] *Ann. Chem.* (Liebig), **210**, 156.

reaction of choranil upon sodium mercaptide, the substitution of chlorine proceeds almost exclusively, if the substances be mixed in water; while if ether be used instead of water, the reaction consists largely of reduction of the quinone to the hydroquinone, with very little substitution. Another case was observed and is described below, in which the use of ether as a solvent caused the formation of one product, while if a different solvent was used, a totally different product was obtained. For the preparation of tetrathioethylquinone, in large quantities, four molecules of potassium hydroxide are dissolved in two parts of water and cooled. Four molecules of mercaptan are mixed with an equal volume of 95 per cent. alcohol, and after cooling, the solution is added to the potassium hydroxide, keeping the temperature below 20°. The chloranil in the proportion of one molecule is boiled with water in a flask, in order to thoroughly wet the substance, and is then cooled to 20°. The mercaptide is now poured into the chloranil and water, and stirred vigorously. The black solid mass is filtered and washed on paper, until the wash-water comes through neutral and colorless, and is then dried in air. Traces of an ill-smelling impurity are removed by mixing the substance with dilute nitric acid (sp. gr. 1.10) to a thin paste, which is to be warmed on the water-bath for half an hour or less, and then filtered, washed with water and recrystallized once from 95 per cent. alcohol. The yield is about 95 per cent. of the theoretical quantity. By acidulating the first aqueous filtrate a small amount of tetrachlorhydroquinone may be obtained. The molecular weight of the substance was determined by the boiling-point method in benzene, and was found to accord with the formula previously given.

Calculated for $C_6(SC_2H_5)_4O_2$.	Found, average of ten determinations.
Mol. wt. = 348.	352.

LEAD SALT OF TETRATHIOETHYLHYDROQUINONE AND ACETIC ACID, $C_6(SC_2H_5)_4(OPbOCOCH_3)_2$.

When pure crystallized tetrathioethylhydroquinone (one molecule) is dissolved in 95 per cent. alcohol and treated with a strong solution of two molecules of lead acetate in alcohol, a yellow crystalline precipitate forms at once in long fibrous needles at low temperatures, changing to less bulky canoe-shaped crystals when warmed, or if formed at a high temperature. The sub-

stance was purified by repeated boiling with small quantities of alcohol containing 2 per cent. acetic acid, followed by thorough washing on the filter with hot alcohol. Lead was determined by suspending the substance in 95 per cent. alcohol and adding dilute sulphuric acid, which dissolved the substance, but precipitated lead sulphate at once. This was washed thoroughly with alcohol, ignited separately, heated with nitric and sulphuric acids in the crucible, and weighed. Sulphur was determined by heating the substance in a sealed tube with fuming nitric acid and a little pure lead nitrate to 260° for six hours. On opening the tube, the contents were evaporated to dryness to remove nitric acid, water was added, and also some pure sodium bicarbonate. After 48 hours, the lead carbonate, thus formed, was filtered and washed, and from the filtrate the sulphur was precipitated as barium sulphate. The lead carbonate precipitate was found to be easily and completely soluble in acetic acid, which served to show that it contained no lead sulphate. The filtrate from the barium sulphate was found to contain no trace of lead, by test with sulphuretted hydrogen.

	Calculated for $C_6(SC_2H_5)_4(OPbOCOCH_3)_2$.	Found. I.	Found. II.
Lead	47.0	46.6	47.4
Sulphur	14.41	14.51	.....

A portion of the substance used for analysis on being gently warmed with dilute sulphuric acid, evolved acetic acid vapors. The substance is formed according to the equation:

$$2Pb(C_2H_3O_2)_2 + C_6(SC_2H_5)_4(OH)_2 = C_6(SC_2H_5)_4(OPbOCOCH_3)_2 + 2HC_2H_3O_2.$$

In one experiment, using 14.5 grams of lead acetate, the acidity of the filtrate was found to be 80 per cent. of the theory. The substance is insoluble in water and in all common solvents, but is slightly soluble in boiling alcohol. It is decomposed by glacial acetic acid, sulphuric, or hydrochloric acids. Suspended in alcohol or ether, and treated with benzoyl chloride, it forms lead chloride and tetrathioethylhydroquinone, but no dibenzoate of tetrathioethylhydroquinone.

On account of its insolubility the formation of this lead salt serves as a delicate test for the presence of tetrathioethylhydroquinone. When a solution of lead acetate in alcohol is mixed with a solution of tetrathioethylquinone in alcohol, no apparent

change occurs, but if one drop of sodium ethylate solution is added, a copious precipitate of this yellow lead salt appears, showing that the reduction is immediate. If lead mercaptide be mixed with lead acetate and chloranil in alcohol, a quantity of this same yellow lead salt is formed, showing that the action of lead mercaptide on chloranil proceeds partly by substitution forming lead chloride, and partly by reduction of the substituted quinone. This yellow lead salt had been obtained on various occasions previously, but only after the completion of the analyses reported above, could any significance be attached to its appearance.

TETRATHIOETHYLHYDROQUINONE DIBENZOATE, $C_6(SC_2H_5)_4(OCOC_6H_5)_2$.

This substance was made and analyzed in December, 1896, but was at that time supposed to be represented by the formula $C_6(SC_2H_5)_4(OCOC_6H_5)_2(SCOC_6H_5)_2$[1] (see Formula III above). For the purposes of this study it was prepared again precisely as in 1896, and used for a molecular weight determination by the boiling-point method in benzene.

Calculated for $C_6(SC_2H_5)_4(OCOC_6H_5)_2)SCOC_6H_5)_2$, mol. wt., 832.
Calculated for $C_6(SC_2H_5)_4(OCOC_6H_5)_2$, mol. wt., 558.
Found: 546, 580, 597, 601, 611, 615, 624, 639.

The substance can be made in various ways. It was first made by mixing sodium mercaptide and $C_6(SC_2H_5)_4O_2$, and benzoyl chloride in ether as previously described. But it can be made with equal ease if sodium ethylate be substituted for the sodium mercaptide, and therefore it cannot contain more than four atoms of sulphur in the molecule. It was made in greater purity and better yield as follows: 11.5 grams of $C_6(SC_2H_5)_4O_2$ were dissolved in glacial acetic acid and reduced by means of zinc dust to the colorless hydroquinone $C_6(SC_2H_5)_4(OH)_2$ as described in the earlier paper. The mixture was poured into water, stirred, filtered, and the mixture of zinc dust and precipitated tetrathioethylhydroquinone was washed with water till neutral. The drained mixture was extracted with 60 cc. of hot alcohol, and to the alcoholic solution thus obtained was added a solution of 1.4 grams sodium in 40 cc. of absolute alcohol. Immediately, more than half a liter of ether was added, which precipitated a solid mass. Eight cc. of benzoyl chloride were stirred in, and the solid dissolved. After evaporating the last traces of ether and

[1] *Am. Chem. J.*, **19**, 293.

alcohol on the water-bath, the residue was digested hot with 10 per cent. aqueous sodium carbonate solution to remove any excess of benzoyl chloride. The oily layer was filtered out, and washed with water, when it solidified rapidly. It was washed with ether to remove traces of coloring-matter, and recrystallized from 95 per cent. alcohol in rhombic plates, varying in form somewhat, when crystallized at different temperatures. The substance having a constant melting-point at 131° was analyzed.

	Calculated for $C_6(SC_2H_5)_4(OCOC_6H_5)_2$.	Found. I.	Found. II.
Carbon	60.21	60.17	59.94
Hydrogen	5.38	5.36	5.90
Sulphur	22.95	23.16	23.07

Mol. wt., 558. 572.1, 531.4, 548.1, 566.8, 584.5; Average, 560.6.

Prepared in this way, the substance was found to be identical in properties with the substance described in the paper referred to, as tetrathioethylquinonedibenzoyldithiobenzoylacetal (formula III above). The percentage compositions calculated from the two formulas are almost identical, but the molecular weights differ widely.

	Calculated for Formula III, $C_6(SC_2H_5)_4(OCOC_6H_5)_2(SCOC_6H_5)_2$.	Calculated for $C_6(SC_2H_5)_4(OCOC_6H_5)_2$.
Carbon	60.57	60.25
Hydrogen	4.81	5.38
Sulphur	23.07	22.95
Mol. wt	832	558

The method of preparation, analyses, molecular weight determinations and the chemical reactions of the substance show that the earlier formula, III, is incorrect, and that the substance is really tetrathioethylhydroquinone dibenzoate.

It is very easily soluble in ethyl acetate, soluble in benzene, ethyl alcohol, or methyl alcohol, nearly insoluble in water, ligroin or 80 per cent. alcohol. It can be recrystallized from benzene or 95 per cent. alcohol. The substance is decomposed by boiling with alcohol and sodium carbonate. Twenty-five per cent. aqueous potassium hydroxide attacks it very slowly at the boiling temperature, but if alcohol be added to the mixture, mercaptan odors are freely evolved and, in six hours, the substance is entirely dissolved. In this respect it differs from the dichlordiethoxyquinonedibenzoyldiethylacetal described by Jackson and Grindley[1] which is stated to be unaffected by boiling alcoholic soda solution.

[1] *Am. Chem. J.*, **17**, 637.

The effect of various solvents in modifying the course of the reactions has already been referred to. Sodium mercaptide acting on dichlordiphenoxyquinone suspended in ether, gave 36 per cent. of the theoretical yield of the substitution-product, $C_6(SC_2H_5)_4O_2$. The same materials mixed in water gave 65 per cent. of the same product.

When a solution of sodium in alcohol is added to tetrathioethylquinone in a little alcohol, the further addition of ether precipitates a yellow solid which probably contains the sodium salt of tetrathioethylhydroquinone. The subsequent addition of benzoyl chloride dissolves the solid, forming the dibenzoate of tetrathioethylhydroquinone, described in this paper. But if the same process be carried out omitting the ether, then benzoyl chloride forms the dibenzoate of dithioethyldiethoxyhydroquinone.

DITHIOETHYLDIETHOXYHYDROQUINONE DIBENZOATE, $C_6(SC_2H_5)_2(OC_2H_5)_2(OCOC_6H_5)_2$.

On dissolving two atoms of sodium in a minimum quantity of absolute alcohol, and adding the alcoholate solution to one molecule of $C_6(SC_2H_5)_4O_2$ moistened with a little alcohol, heat is evolved, the mass turns brown, and all dissolves. If the bulk of alcohol be small, a granular crystalline precipitate soon separates which is easily soluble in alcohol. On adding to this mixture two molecules of benzoyl chloride, much heat is evolved and the solid dissolves. After removing alcohol by evaporation, and the excess of benzoyl chloride by the use of hot aqueous sodium carbonate solution, the oily residue is washed with water and made to crystallize by adding a little warm alcohol. The substance is difficultly soluble in 95 per cent. alcohol, is insoluble in water, ligroin or 80 per cent. alcohol. It is soluble in benzene, chloroform or ether. It can be recrystallized from glacial acetic acid, or better from ethyl acetate. It forms equilateral six-sided plates and melts at 184-184.5°. Analysis gave the following results:

	Calculated for $C_6(SC_2H_5)_2(OC_2H_5)_2(OCOC_6H_5)_2$.	Found. I.	Found. II.
Carbon	63.87	64.21	64.62
Hydrogen	5.70	5.70	5.95
Sulphur	12.16	12.45	11.92
Mol. wt.	526	587	

The substance is not affected by boiling with sulphuric acid of specific gravity 1.40.

As a result of the work here reported, the following conclusions have been reached:

(1) The action of the mercaptides of lead and sodium on the quinones used consists of substitution and of reduction, and no addition-products have as yet been isolated.

(2) The substance described as an addition-product in the paper referred to, under the name tetrathioethylquinonedibenzoyldithiobenzoylacetal, does not possess the formula there assigned to it, but is really the dibenzoate of tetrathioethylhydroquinone, a reduction-product of tetrathioethylquinone.

(3) It was shown that the solvent used determines or largely modifies the course of several reactions between the substances under examination.

(4) By the selection of a suitable solvent and in other ways, the method of making tetrathioethylquinone, was improved so that 95 per cent. of the theoretical yield can now be obtained instead of 10 per cent. or less by the older methods.

(5) The preparation, solubilities and analysis of the dibenzoate of tetrathioethylhydroquinone (m. p. 131°), of the lead double salt of acetic acid and tetrathioethylhydroquinone and of the dithioethyldiethoxyhydroquinone dibenzoate (m. p. 184-184.5°) are here described.

In conclusion, I wish to express my thanks to Professor H. S. Grindley, of the Department of General Chemistry, for permission to undertake this work, in a field of research previously entered by himself.

UNIVERSITY OF ILLINOIS,
URBANA, ILLINOIS.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 107.]

THE CONDENSATION OF SUCCINYLOSUCCINIC ACID DIETHYL ESTER WITH GUANIDINE. A DERIVATIVE OF 1,3,5,7-NAPHTTETRAZINE, A NEW HETEROCYCLE.[1]

BY MARSTON TAYLOR BOGERT AND ARTHUR WAYLAND DOX.

Received July 21, 1905.

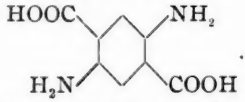
IN extending the work upon the quinazoline compounds, which has been going on in this laboratory for several years,[2]

[1] Read at the meeting of the New York Section of the American Chemical Society, April 7, 1905.

[2] This Journal, **22**, 129, 522 (1900); **23**, 611 (1901); **24**, 1031 (1902); **25**, 372, 935 (1903); **27**, 649 (1905).

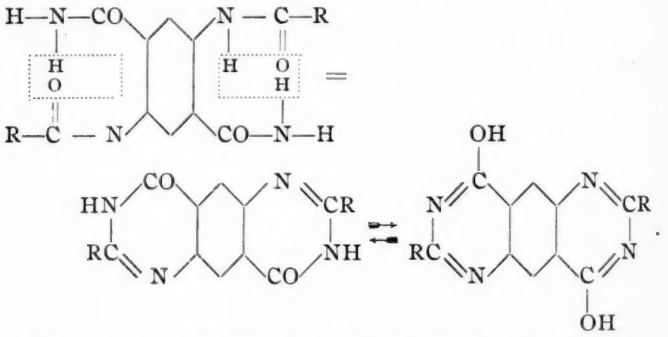
it was decided to conduct some experiments with *p*-diaminoterephthalic acid, in the hope of obtaining naphttetrazines therefrom by the usual quinazoline condensations.

If *p*-diaminoterephthalic acid has the structure generally assigned to it, it contains the anthranilic acid grouping twice, as a glance at its constitutional formula will show:

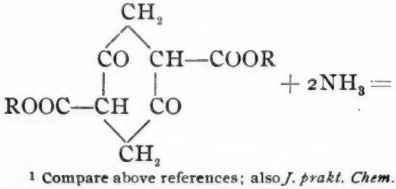


It might, therefore, be expected to give the usual anthranilic acid reactions and condensations.

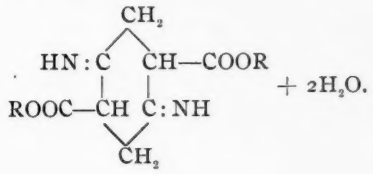
Most of the quinazoline syntheses from anthranilic acids depend upon the intermediate formation of acylated anthranilamides, which then pass into the quinazolines by loss of water and ring closure. *p*-Diaminoterephthalic acid should give a naphttetrazine by such a condensation.[1]

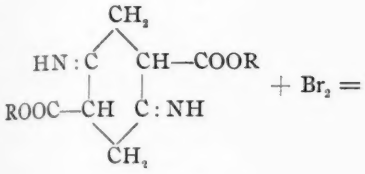


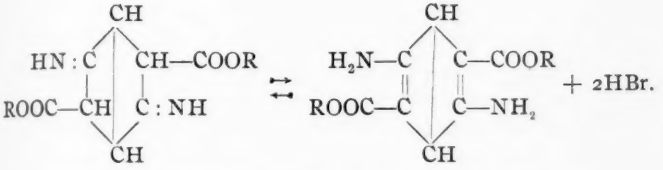
p-Diaminoterephthalic acid was prepared from succinylosuccinic ester by converting the ester into the diimine, oxidizing the latter in concentrated sulphuric acid solution with bromine, and saponifying the resultant diaminoterephthalic ester. The reactions are as follows:



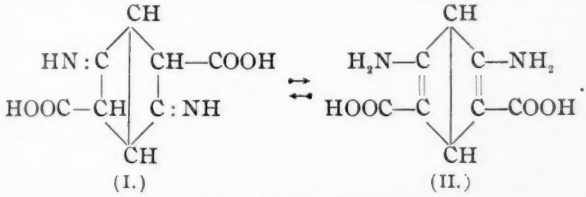
[1] Compare above references; also *J. prakt. Chem.* [2], **36**, 143 (1887); *Ibid.*, **40**, 1 (1889); *Ibid.*, **51**, 564 (1895); *Ber.*, **26**, 1349 (1893); *Ibid.*, **35**, 3480 (1902); etc.







Saponification of the ester then gives the free acid:



(I.) (II.)

This is the method of Baeyer[1] and Böninger.[2] Geuther[3] was of the opinion that the succinylosuccinic ester diimine possessed the tautomeric structure and was a true diaminodihydroterephthalic ester. Hantzsch and Hermann[4] assigned to the orange-red diaminoterephthalic ester the quinoid structure (I), because of its color, and to the salts with mineral acids, all of which are colorless, the diamino structure, the presence of the mineral acid inducing the change of the imino to the more basic amino group. Böninger,[5] for similar reasons, assigned the quinoid structure to the yellowish green, free diaminoterephthalic acid, and the

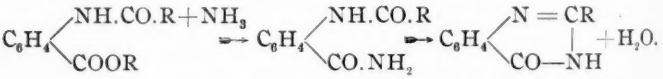
[1] *Ber.*, **19**, 430 (1886).
[2] *Ibid.*, **21**, 1765 (1888).
[3] *Ann. Chem.* (Liebig), **244**, 213.
[4] *Ber.*, **21**, 1755 (1888).
[5] *Loc. cit.*

diamino structure to its colorless salts with strong mineral acids. In giving the structure of the diamino tautomer (II), I have retained the para bond. This formula illustrates most simply the migration of hydrogen from carbon to nitrogen, and involves no readjustment of the binding. Further, it is not impossible that this may represent the true structure of the compound, and be the cause of some of its peculiar reactions.

In the preparation of the diimine from succinylosuccinic ester and ammonium acetate, Baeyer[1] recommends using 10 parts of acetate to 1 of ester, and working on small amounts (1 gram at a time). We have found that half as much acetate gives fully as good results, in fact we have occasionally used 2 parts of acetate to 1 of ester without noting any great difference in the yield or purity of the product; and further, 100 grams of ester can be converted into diimine just as readily as 1 gram. By repeated crystallization of the diimine from various solvents, we could not raise its melting-point above 177-178° (corr.). Baeyer gives it as 181°. If the fusion with ammonium acetate is properly conducted, the first product is practically pure and can be converted directly into the diaminoterephthalic ester.

The oxidation of succinylosuccinic ester diimine to *p*-diaminoterephthalic ester by bromine, in concentrated sulphuric acid solution, proceeds most satisfactorily at 40-50°, and is complete in about half an hour. The diamino ester is precipitated as sulphate, from which the ester is liberated by the action of sodium acetate.

Weddige[2] has prepared quinazolines by heating acylanthranilic esters with alcoholic ammonia at 150-160°:



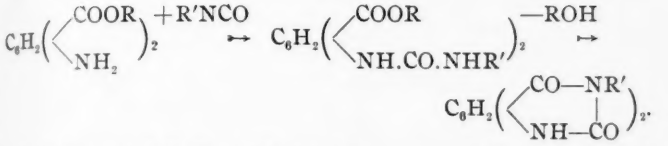
Attempts to prepare acyl derivatives of diaminoterephthalic ester were unsuccessful, so that the above condensation could not be realized.

The diamino ester reacts with phenyl isocyanate and with phenyl isothiocyanate, but the character of the products is still undetermined. The reaction should proceed as follows:[3]

[1] *Loc. cit.*

[2] *J. prakt. Chem.* [2], **36**, 155 (1887).

[3] Compare Söderbaum and Widman: *Ber.*, **22**, 1669 (1889); Stewart: *J. prakt. Chem.* [2], **44**, 415 (1891); Wielandt: *Ibid.* [2], **49**, 319 (1894); etc.

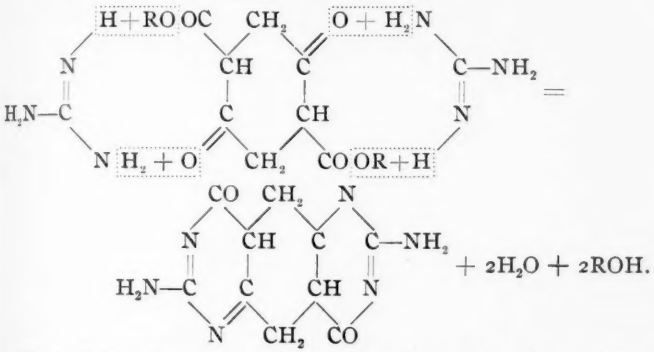


p-Diaminoterephthalic acid may be prepared in any desired amount, with ease and rapidity, by the process outlined. It is exceedingly inert and insoluble. All attempts to obtain ortho condensations from it were futile. Acid anhydrides, formamide,[1] urea,[2] thiourea,[3] and phenylisothiocyanate had no action upon it.

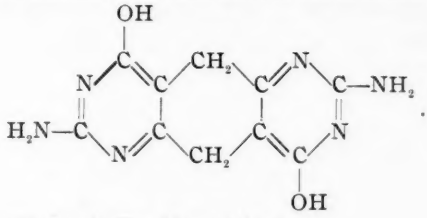
The study of *p*-diaminoterephthalic acid and its derivatives is being continued and the results will be communicated later.

The experiments with *p*-diaminoterephthalic acid having resulted so unsatisfactorily, we sought by another path to reach the same goal, and, by condensing guanidine with succinylosuccinic ester, achieved our purpose.

The condensation may be expressed thus:

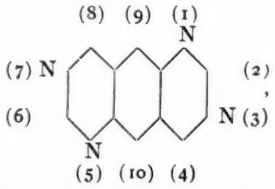


The sodium salt may be a derivative of the tautomeric enol form:

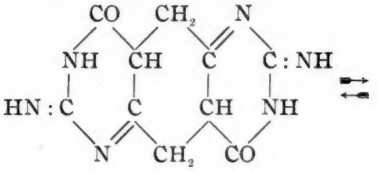


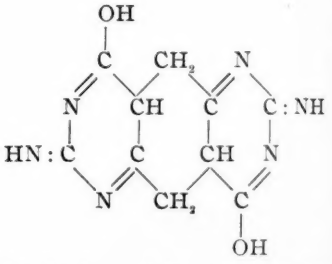
[1] Niementowski: *J. prakt. Chem.* [2], **51**, 564 (1895).
[2] Niementowski: *Ibid.* [2], **40**, 1 (1889).
[3] Stewart: *Loc. cit.*

The latter would be a mesodihydro derivative of the 1,3,5,7-naphttetrazine heterocycle,



and might be designated 2,6-diamino-4,8-dihydroxy-9,10-dihydro-1,3,5,7-naphttetrazine. It is possible, on the other hand, that the guanidine reacts with both its primary amino groups, leaving the imino group unaffected. The configuration would then be:



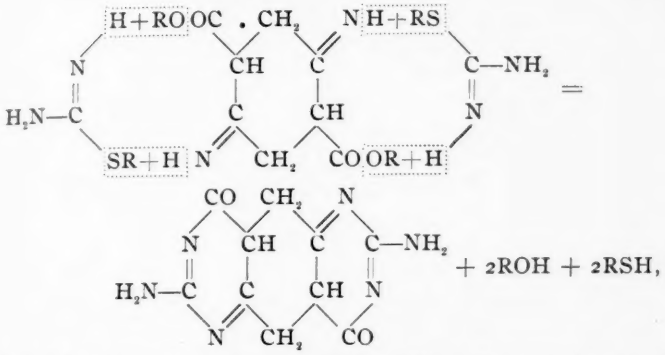


Other possible tautomers would arise by a different wandering of the hydrogens in the two —C(:NH)—NH—CO—CH: groupings. Which of these formulas correctly represents the structure of the condensation-product cannot yet be stated positively. Further experiments in this direction are under way.

The compound is an interesting one, as no similar heterocycles have ever been prepared so far as we can ascertain. Perhaps the nearest approach to it is the benzodipyrazolon obtained by condensing succinylosuccinic ester with hydrazine hydrate.[1]

We also endeavored to prepare the naphttetrazine from a pseudothiourea and succinylosuccinic ester diimine, thus,

[1] *J. prakt. Chem.* [2], **51**, 64 (1895).

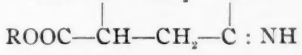


but the attempt was unsuccessful, although mercaptan was evolved in the reaction.

The naphttetrazine is characterized by great insolubility, infusibility, and inertness. It forms a yellow crystalline sodium salt, which possesses a beautiful green fluorescence.

EXPERIMENTAL PART.

Succinylosuccinic Acid Diethyl Ester Diimine,



—This was prepared, by a modification of the Baeyer method,[1] from succinylosuccinic ester and ammonium acetate. The reaction is an interesting one to watch.

One part of the ester is mixed with 5 parts of dry ammonium acetate, in a strong round-bottomed flask, and the mixture melted down carefully over the naked flame. The melted ester appears as clear, yellow, oily drops floating about in the colorless, water-clear ammonium acetate. After heating the melt for a few moments it begins to "crackle" (presumably from separation of water). This crackling soon ceases, and in a minute or two the liquid suddenly boils up vigorously (the flame should be removed for a few seconds, or the boiling may become too violent). Simultaneously, the yellow oily drops of ester solidify to pale yellow lumps of the diimine, which swim about in the liquid. The boiling should not be continued more than a minute or two longer to complete the reaction.

[1] *Loc. cit.*

Baeyer heated the mixture of ester and acetate until a clear yellow solution resulted. This he says, took about a minute, when he used 1 gram of the ester to 10 of acetate. Our experience showed that it was inadvisable to continue heating until complete solution resulted, and that the best time to stop was a minute or two after the melted ester had changed to the solid diimine. It is quite true that if the mixture be boiled down rapidly over the free flame, all of the solid will gradually dissolve (using 25 grams of ester, it took fifteen minutes vigorous boiling before a clear solution resulted), but the color of the melt gradually changes from a light yellow to a dark olive-green or even to an olive-brown, and the product is darker-colored and less pure.

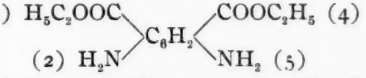
Upon the completion of the reaction, the melt is allowed to cool, with occasional shaking to prevent the formation of large crystals. A solid cake of ammonium acetate results, containing amorphous pale yellow lumps and light yellow crystals of the diimine, the crystals representing the diimine which was held in solution by the molten ammonium acetate. The cake is crushed up and washed thoroughly with cold water. The diimine remains undissolved as a pale yellow solid, practically pure, and in nearly quantitative yield. By crystallization from alcohol, it may be obtained in beautiful light yellow needles, but the crude product is sufficiently pure for direct conversion into *p*-diaminoterephthalic ester.

In spite of repeated crystallizations from various solvents, the melting-point of the diimine could not be raised above 177-178° (corr.). Baeyer gives it as 181°. It is apparently insoluble in cold water, very difficultly soluble on boiling; very difficultly soluble in dry ether, carbon disulphide, or naphtha; very difficultly soluble in cold carbon tetrachloride, difficultly soluble on boiling; difficultly soluble in cold glacial acetic acid, easily soluble on boiling; moderately soluble in cold absolute alcohol, but dissolves readily on boiling; difficultly soluble in cold ethyl nitrate, easily soluble on boiling; easily soluble in chloroform, acetone, benzene, nitrobenzene, aniline, or ethyl acetate. It crystallizes well from absolute alcohol, ethyl nitrate, or from a mixture of chloroform and naphtha. It is not readily decomposed by boiling with dilute caustic potash, ammonia being evolved very slowly. It is moderately soluble in cold concentrated sulphuric acid, and on diluting this solution a white precipitate separates

(probably the sulphate). We have also endeavored to prepare the diimine by passing dry ammonia gas into various solutions of succinylosuccinic ester, but the results were generally unsatisfactory.

An attempt was made to prepare a naphttetrazine by the action of a pseudothiourea upon this diimine. One molecule of the diimine and two of pseudomethylthiourea hydriodide were dissolved in warm 95 per cent. alcohol, two molecules of sodium ethylate added, and the mixture boiled seven hours under a return condenser. The odor of mercaptan was evident, but no precipitate separated, and, on cooling, the diimine crystallized out unchanged. The boiling was then continued for seven hours longer, but no naphttetrazine could be detected in the product.

p-Diaminoterephthalic Acid Diethyl Ester,



—Succinylosuccinic ester diimine was oxidized to diaminoterephthalic ester by dissolving the diimine in concentrated sulphuric acid and adding bromine, as recommended by Baeyer.[1] The oxidation proceeds very satisfactorily at 40-50°, but the "clouding" of the solution, which Baeyer gives as the indication of the completion of the reaction, was not observed. Although we continued the oxidation much longer than he, the solution remained quite clear, with excess of bromine undissolved. The oxidation is apparently complete in half an hour. The solution is then decanted from excess of bromine, the bromine in the solution blown out by a stream of dry air, and the liquid poured upon cracked ice wet with sulphurous acid. The difficultly soluble sulphate of the diamino ester separates as a white precipitate. The mixture is left in an ice pack for an hour or two, the precipitate filtered out, washed well with ice water, suspended in a small amount of water and treated with saturated sodium acetate solution, whereby the free ester is separated as an orange-yellow flocculent precipitate. When dry, it forms an orange-yellow powder. On adding this dry ester to boiling absolute alcohol, it immediately turns a brilliant red and dissolves, crystallizing from the solution on cooling in orange-red prisms, about the color of potassium dichromate. Frequently,

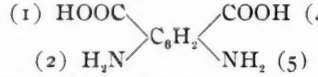
[1] *Loc. cit.* In the oxidation of succinylosuccinic ester itself to dihydroxyterephthalic acid, concentrated sulphuric acid appears to be just as good a solvent as carbon disulphide.

it separates in light yellow crystals of similar habit, which, on recrystallization, change to the orange-red variety. This dimorphism was first reported by Häussermann and Martz.[1] The ester is apparently insoluble in water or naphtha; difficultly soluble in ether, carbon tetrachloride, carbon disulphide, cold absolute alcohol, cold benzene, or cold ethyl acetate; moderately soluble in the last three solvents at their boiling-points, in cold acetone, cold glacial acetic acid, cold nitrobenzene, cold aniline, or cold ethyl acetate; easily soluble in the five latter solvents at their boiling-points, or in chloroform. Its solutions are generally golden brown with a yellow fluorescence.

Some of the ester was treated with excess of acetic anhydride. Heat was evolved and the ester gradually dissolved, but no acetyl derivative could be isolated from the product. Fusion of the ester with urea or with thiourea likewise gave negative results.

The ester reacts with phenyl isocyanate and with phenyl isothiocyanate, and the general behavior of the products is much like that of the naphttetrazine described beyond. Further work upon the subject is requisite, before their nature can be positively stated. The product obtained with phenyl isothiocyanate is yellow, very difficultly soluble in water, absolute alcohol, amyl alcohol, amyl acetate or valerate, ethyl nitrate, naphtha, ether, chloroform, carbon tetrachloride, carbon disulphide, acetone, xylene, or nitrobenzene, but dissolves in phenol, aniline, pyridine, or quinoline. The solutions all show a strong yellowish green fluorescence. It dissolves in caustic or carbonated alkali or in ammonium hydroxide, and is reprecipitated from these solutions by acids.

p-Diaminoterephthalic Acid,



was prepared by saponifying the above ester.[2] It is not necessary to use the free ester for this purpose; the sulphate of the ester obtained in the above oxidation of succinylosuccinic ester diimine will do just as well. By boiling this sulphate with excess of aqueous alkali, and precipitating with acetic acid, the diamino acid is obtained as a yellowish green micro-crystalline

[1] *Ber.*, **26**, 2984 (1893).
[2] Böninger: *Loc. cit.*

solid. It may be purified by dissolving in alkali and reprecipitating with acetic acid. It is insoluble in all ordinary solvents except glycerol and caustic alkalies. It is infusible and exceedingly inert. Boiling acetic anhydride had no appreciable effect upon it, nor could an acetyl derivative be obtained through its silver salt.[1] The silver salt was suspended in dry ether and treated with acetyl chloride; it was also heated with acetyl chloride for six hours in a sealed tube at 150°, but in neither case did any reaction occur. The acid was not attacked by boiling phenyl isothiocyanate. Fusions with formamide,[2] with urea,[3] or with thiourea[4] were also fruitless. At high temperature, the acid decomposes with formation of a small amount of substance which gives the reactions of *p*-phenylenediamine.

REACTIONS WITH SUCCINYLOSUCCINIC ESTER.

Behavior of Succinylosuccinic Ester with Urea, and with Phenyl Isocyanate.—Succinylosuccinic ester and urea were boiled together in absolute alcohol solution, but no reaction ensued. Fused zinc chloride was then added to the solution, but its only effect was to form a yellow, insoluble zinc compound with the ester, which was decomposed by concentrated hydrochloric acid into zinc chloride and the ester again. Fusion of the ester with urea also failed to induce any condensation.

Succinylosuccinic ester dissolves freely in hot phenyl isocyanate, and crystallizes out unchanged on cooling.

Succinylosuccinic Ester and Guanidine Salts.—One molecule of succinylosuccinic ester and two of guanidine thiocyanate were dissolved in absolute alcohol, and the solution boiled six hours under a return condenser. On cooling, practically all the ester crystallized out unchanged. The mixture was again heated and two molecules of sodium ethylate added. The surface of the ethylate instantly changed to a bright red, the solution turned yellow, and a yellowish white precipitate separated. The ethylate rapidly dissolved and the precipitate gradually increased in amount. After boiling for three hours, the solution was filtered hot, and the precipitate washed with alcohol. It is sufficiently soluble in alcohol to give a red color with ferric chloride solution, but this color is not soluble in ether. The precipitate, when dry,

[1] Wheeler: *Am. Chem. J.*, **20**, 222.
[2] Niementowski: *J. prakt. Chem.* [2], **51**, 564 (1895).
[3] Niementowski: *Ibid.*, **40**, 1 (1889).
[4] Stewart: *Loc. cit.*

appeared as a yellow powder. It was purified through its sodium salt. The purified salt was dissolved in hot caustic soda, and excess of hydrochloric acid added, to precipitate the white hydrochloride. This was treated, without filtering, with excess of ammonium hydroxide. The free base then appeared as a yellow flocculent precipitate. On careful heating, a slight yellow sublimate was obtained, but most of it charred and gave off a strong odor of ammonia. It is apparently insoluble in water, glycerol, ether, ethyl acetate, amyl valerate, acetone, carbon disulphide, chloroform, carbon tetrachloride, benzene, nitrobenzene, aniline, phenol, pyridine, or quinoline. In alcohol, its solubility is only sufficient to give the color reaction with ferric chloride. It dissolves freely in dilute caustic alkalies, but is reprecipitated by the addition of concentrated alkali. It is soluble in concentrated nitric or sulphuric acids, but not in concentrated hydrochloric acid. Its solution in concentrated sulphuric acid is reprecipitated by sodium acetate. It dissolves also in glacial acetic acid, and is reprecipitated by the addition of ammonium hydroxide but is redissolved by excess of the precipitant.

The purified free base was analyzed with the following results: Found: C, 48.56, 48.68; H, 4.16, 4.12; N, 32.54, 32.16, 32.30, 32.63. Calculated for $C_{10}H_{10}O_2N_6$; C, 48.78; H, 4.06; N, 34.15.

It will be noted that the figures for nitrogen are nearly 2 per cent. too low. The reason for this we do not know. The nitrogen was determined by various methods, but the results were invariably too low. We found some comfort, however, upon examining the literature, to see that other experimenters, dealing with similar heavy molecules very rich in nitrogen, have had similar troubles. That our product is really a naphttetrazine seems fairly well established by the other analytical results, both for the free base and for its sodium salt, and, further, by the fact that we have recently prepared a similar condensation product from succinylosuccinic ester and acetamidine, the analysis of which resulted much more satisfactorily[1].

Hydrochloride.—This is colorless, insoluble in hydrochloric acid, and less stable than the sulphate, being dissociated by water.

Sulphate.—The free base was dissolved in concentrated sulphuric acid, the solution diluted carefully and allowed to stand some time.

[1] A paper will shortly appear on this condensation-product.

The sulphate gradually separated as a colorless crystalline precipitate, composed of beautiful, microscopic, glassy rhombohedra.

Sodium Salt.—The free base dissolves very easily in dilute caustic soda, but the sodium salt thus formed is insoluble in the strong alkali. The base is, therefore, suspended in water, brought into solution by the addition of a little concentrated caustic soda, and the solution heated to boiling. Concentrated caustic soda is run in until the sodium salt begins to separate in the boiling solution. The heating is then stopped, and, on cooling, all the sodium salt crystallizes out in yellow needles or prisms. The alkaline solution of the crude base turns red in the air, but this is apparently due to a small amount of impurity, as after several recrystallizations from caustic soda the alkaline solution no longer shows this behavior. The pure salt forms light yellow crystals with a beautiful green fluorescence. Its aqueous solution shows the same fluorescence, but the addition of strong caustic soda precipitates it so completely that not a trace of fluorescence remains in the mother-liquor, while the separated crystals are strongly fluorescent.

The crystals contain six molecules of water of crystallization. They are quite stable in the air, and lose water when washed with absolute alcohol. In aqueous solution it evidently dissociates. It is decomposed by acids. It is very difficult to purify, the best agent for washing the crystals free from the alkaline mother-liquor being 95 per cent. alcohol, but even this appears to cause some dissociation.

The water of crystallization was determined with the following result: Water found, 27.70, 27.71. Calculated for $C_{10}H_8O_2N_6Na_2 \cdot 6H_2O$, 27.14.

The dried substance was then analyzed for sodium: Na found, 15.10, 15.14. Calculated for $C_{10}H_8O_2N_6Na_2$, 15.86.

The alkaline solution of the sodium salt gives no precipitates with alkaline solutions of lead, aluminum, or zinc salts, but is precipitated by carbon dioxide or acetic acid, the precipitate redissolving in excess of acetic acid.

Potassium Salt.—This was prepared in the same way as the sodium salt. Crystallized from caustic potash, it forms needles of a paler yellow than the sodium salt. It is much more soluble in strong alkali than the latter, and hence still more difficult to purify.

Guanidine acetate, used instead of the thiocyanate, gave the same condensation-product.

An attempt was made to prepare the naphttetrazine by direct fusion of succinylosuccinic ester and guanidine acetate, in the same way that the diimine was made from succinylosuccinic ester and ammonium acetate, but no condensation occurred.

Finally, a solution of free guanidine was prepared from the carbonate and condensed with succinylosuccinic ester, but this variation showed no advantage over the use of a guanidine salt and sodium ethylate either in the yield or purity of the product.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, NO. 90.]

DOUBLE FLUORIDES OF TANTALUM.[1]

BY CLARENCE W. BALKE.

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THE results set forth in this article constitute a chapter in the reinvestigation of the compounds of columbium and tantalum now in progress in this laboratory. While partly confirmatory in nature, they mark a distinct advance in certain directions, and, it is hoped, will materially aid in a continuation of the investigation.

Berzelius[2] first prepared and analyzed the potassium salt, $2KF.TaF_5$. In addition he mentioned a calcium, a magnesium, and a lead salt, and further, a potassium salt containing as much as 63 per cent. of tantalic acid, and an ammonium salt, but these were not analyzed, nor were any formulas assigned to them.

H. Rose[3] prepared and analyzed the potassium salt and also the 3:1 sodium salt, $3NaF.TaF_5$.

Marignac,[4] in 1866, published the most complete investigation of these salts which has been made up to the present time. He studied the ammonium, potassium, sodium, zinc and copper salts.

A. Joly[5] described an ammonium oxyfluoride of tantalum of the

[1] From author's thesis presented to the University of Pennsylvania for the Ph.D. degree.

[2] *Pogg. Ann.*, **4**, 6 (1825).

[3] *Ibid.*, **99**, 481 (1856).

[4] *Bibl. Univ. Arch.*, **26**, 89; *Ann. ch. Phys.* [4], **9**, 247 (1866).

[5] *C. R.*, **81**, 1266 (1875).

composition $3NH_4F.TaOF_3$. No analyses were given, and the existence of such a salt cannot be considered as well established.

A. Piccini[1] prepared and analyzed a potassium tantalum double fluoride of the composition, $2KF.TaO_2F_3.H_2O$.

Finally, Mary Engle Pennington[2] prepared the rubidium salt, and a caesium salt to which the composition, $15CsF.TaF_5$, was assigned. This latter salt was not encountered by the writer.

The existence of the following double fluorides may be considered as beyond question:

$2NH_4F.TaF_5$
$2KF.TaF_5$
$2KF.TaO_2F_3.H_2O$
$3NaF.TaF_5$
$2NaF.TaF_5.H_2O$
$2RbF.TaF_5$
$ZnF_2.TaF_5.7H_2O$
$CuF_2.TaF_5.4H_2O$

In the present study a number of them have been reinvestigated, and the following new salts have been obtained:

$LiF.TaF_5.2H_2O$
$NaF.TaF_5$
$CsF.TaF_5$
$2CsF.TaF_5$
$C_5H_5N.HF.TaF_5$
$3(C_5H_5N.HF).2TaF_5.2H_2O$

MATERIAL.

The tantalic oxide used in the preparation of these salts was obtained from the columbite of South Dakota, large amounts of which have been worked up in this laboratory by R. D. Hall.[3] The potassium tantalum fluoride, obtained as a crystalline precipitate upon the addition of potassium fluoride to the hydrofluoric acid solution of the mixed metallic oxides, was purified in the following manner. About 2300 grams of the salt were recrystallized from water containing enough hydrofluoric acid to prevent the formation of an oxy-salt. At first considerable difficulty was encountered in making the solutions and filtrations, due to the comparative insolubility of the salt, and its rapid

[1] *Z. anorg. Chem.*, **2**, 21 (1892).
[2] This Journal, **18**, 38 (1896).
[3] *Ibid.*, **26**, 1235 (1904).

separation in the funnel. However, with the large platinum and rubber dishes provided for the purpose, this difficulty was soon overcome.

The salt was brought into solution in a 5 liter platinum dish,[1] and when the solution had become saturated at a temperature not far below its boiling-point, it was decanted through a large rubber funnel surrounded by boiling water. The solution was collected in hard rubber dishes, having a capacity of about 5 liters, and allowed to cool. The crystals which separated were removed, and the mother-liquor was returned to the large platinum dish to be again saturated with the salt. In this way the necessity of evaporating the solutions was eliminated. The potassium columbium oxyfluoride and other impurities concentrated in the mother-liquor, and after the entire amount of salt had passed through the solution in the manner just indicated, about 200 grams of salt were finally discarded in the mother-liquor. These crystallizations were repeated three times, and at the completion of each crystallization, a large amount of salt was allowed to remain in the mother-liquors. The mother-liquor from the first crystallization contained considerable potassium columbium fluoride, while that from the last crystallization was practically free from columbium.

The potassium tantalum fluoride obtained in this way was now free from impurities with the exception of silica, it being impossible to remove this impurity by crystallization alone. The salt, in 500-gram lots, was mixed with at least twice its weight of concentrated sulphuric acid and heated in a 3-liter platinum dish over a battery of four Bunsen burners. The heating was continued until the mass had assumed the consistency of a thick paste. By this treatment any silica present must have been eliminated. The mass was next boiled up repeatedly with large amounts of water, and the white oxide obtained was repeatedly washed by decantation.

The purity of this oxide was tested as follows. The first extract obtained after the treatment of the potassium tantalum fluoride with sulphuric acid was examined for iron, with negative results. Twenty-five grams of the oxide were fused with sodium carbonate and sulphur, and the aqueous extract of the fusion was examined for tin and tungsten, again with negative results. A

[1] The dish consisted of a platinum lining supported by a nickel shell.

potassium binoxalate solution of its hydrate gave no coloration with hydrogen peroxide, indicating the absence of titanium.

Tantalum oxide prepared in this manner dissolved readily in aqueous hydrofluoric acid to a clear solution, which served for the preparation of the double fluorides to be described.

All of the hydrofluoric acid used in the present investigation was carefully distilled from a platinum retort, potassium hydroxide being added to hold back any silica in the commercial acid.

LITHIUM SALT.

$LiF.TaF_5.2H_2O$.—Though difficultly soluble in water, lithium fluoride was found to dissolve quite readily in a strong hydrofluoric acid solution of hydrofluotantalic acid. In the preparation of the above salt 40 grams of tantalic oxide were dissolved in strong hydrofluoric acid, and to this solution 10 grams of lithium carbonate were added. A clear solution resulted and this, after concentration on the water-bath and subsequent cooling, deposited colorless crystals, which were found to have the composition indicated above. They were recrystallized with ease from strong hydrofluoric acid. On standing in the air, the crystals gradually lost their luster. This was observed to be generally true with the double fluorides which contained water of crystallization, while the anhydrous salts retained their brilliancy for months.

Analysis.—The salt was weighed into a platinum crucible and covered with several times its weight of concentrated sulphuric acid. The crucible was heated gently at first, and then more strongly until the greater part of the acid had been expelled. The mass was then boiled up with water and the tantalum oxide filtered out. It was often noticed that this precipitate decrepitated upon ignition, so that care had to be exercised in order to prevent loss of material. The filtrate from the tantalum oxide was evaporated in a platinum crucible, and the latter was then ignited, the lithium being weighed as sulphate. With one of two exceptions to be noted later, this method of analysis was employed for all of the double fluorides of tantalum with the alkali metals.

To determine the water, the salt was mixed with lead oxide and carefully ignited, the water being collected in a weighed calcium chloride tube.

		Calculated for $LiF.TaF_5.2H_2O$. Per cent.	Found. Per cent.
LiF	26	7.65	7.82
TaF_5	278	81.76	80.98
$2H_2O$	36	10.59	10.80
	340	100.00	99.60

Crystallography.[1]—The salt crystallized in the monoclinic system. The crystal habit was quite simple, as may be observed from the accompanying figure. The clinodome (012) was ob-

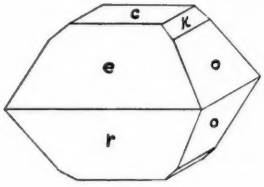

Fig. 1.

served on only a few of the crystals. The latter were several mm. in diameter, but their faces were not sufficiently smooth to admit of the most accurate measurement. The measurements chosen as fundamental are indicated by an asterisk.

MONOCLINIC AXES $\dot{a} : \overset{+}{b} : \overset{1}{c} = 0.5703 : 1 : 1.6235$. $\beta = 87° 46'$.

		Measured.	Calculated.
co,	$001 \wedge 011 =$	$*58° 21'$	
ce,	$001 \wedge 101 =$	$*68° 40'$	
er,	$101 \wedge 10\bar{1} =$	$*38° 41'$	
ck,	$001 \wedge 012 =$	$38° 59'$	$39° 3'$
ok,	$011 \wedge 012 =$	$19° 22'$	$19° 18'$
cr,	$001 \wedge \bar{1}01 =$	$72° 36'$	$72° 39'$
eo,	$\bar{1}01 \wedge 011 =$	$79° \frac{1}{2}'$	$78° 59\frac{1}{2}'$
ro,	$\bar{1}01 \wedge 011 =$	$80° 47'$	$81°$

SODIUM SALTS.

Two double fluorides of sodium and tantalum have been described, $3NaF.TaF_5$ and $2NaF.TaF_5.H_2O$. Marignac prepared them by dissolving sodium tantalate, $3Ta_2O_5.4Na_2O.24H_2O$, in hydrofluoric acid and concentrating the solution. The first crops constituted the 3 : 1 salt, and their removal left a mother-liquor

[1] The author wishes to take this opportunity to express his thanks to Professor Amos P. Brown for many valuable suggestions in connection with the crystallographic part of this investigation.

richer and richer in tantalum fluoride, until finally the 2:1 salt crystallized out.

$3NaF.TaF_5$.—This is the characteristic double fluoride of tantalum with sodium. It is produced when the 2:1 salt is recrystallized, the latter being formed only in the presence of an excess of tantalum fluoride. In the present instance sodium fluoride and tantalum fluoride were mixed in the proportion of 4:1, and the solution was concentrated on the water-bath. On cooling, the above salt separated in rather indistinct forms, which, however, on recrystallization from water containing a small amount of hydrofluoric acid, separated in well formed, exceedingly brilliant, orthorhombic crystals. This salt was more stable than the 2:1 potassium salt, being soluble in boiling water without the separation of an oxy-salt, but as hydrofluoric acid was lost in the escaping vapor, it was always recrystallized from water containing some acid. When the dry salt was heated in a platinum crucible, it decrepitated, fused to a clear liquid, and slowly decomposed on stronger heating.

Its solubility was determined as follows: A saturated solution of the salt was obtained by allowing the crystals to remain in contact with the solution in a rubber beaker for several hours, the solution being stirred from time to time. The clear liquid was decanted into a weighed platinum dish and the latter reweighed. The solution was then evaporated to dryness on the water-bath, a few drops of hydrofluoric acid being added when the evaporation had become nearly complete. The dish with the dry salt was again weighed. Two determinations were made, in which 1 gram of the salt was found to dissolve in 20.9 and in 20.5 parts of water at 25° C.

When titrated with an alkali, the point of neutrality was reached at the completion of the reaction

$$3NaF.TaF_5 + 5NaOH = Ta(OH)_5 + 8NaF.$$

0.4861 gram required 37.2 cc. of a solution of sodium carbonate, 1 cc. of which contained 0.0038 gram of sodium, which corresponds to 24.03 per cent. of fluorine, that calculated for 5F being 23.51 per cent.

The analysis of this salt was conducted as in the case of the lithium salt. In the following table the results obtained by H. Rose and Marignac are included.

	Calculated for $3NaF.TaF_5$.		I.	II.	H. Rose.		Marignac.		
3NaF	126	31.19	31.28	31.32	30.28	32.61	31.26	31.29	
TaF_5 .	278	68.81	68.45	68.61	67.22	67.46	68.68	67.66	69.19
	404	100.00	99.73	99.93	97.50	100.07	99.94	.98.95	
7F ..	152	37.62					37.83		

Crystallography.—The form of this salt is orthorhombic. It showed a marked monoclinic aspect, and was thought at first to belong to the monoclinic system. Careful measurements, however, proved that the a axes and c axes would be of equal length if the crystals were referred to the latter system, and further, the crystals were observed to extinguish parallel to the face *a* (see figures). Many of the crystals grew out into the solution in the form of apparent six-sided prisms due to an elongation parallel to the axis of a zone containing two prisms and four pyramid faces. Such a crystal is shown in Fig. 4, and this seems to be the characteristic habit of the salt, though some crystals were observed with terminations on both ends. Fig. 2 is a projection on the plane of the lateral axes and indicates the relative positions of the faces, while Fig. 3 is a similar projection of an actual crystal.

In many of the crystals the faces of the pyramid (131) were but slightly developed or entirely absent. The best crystals were ob-

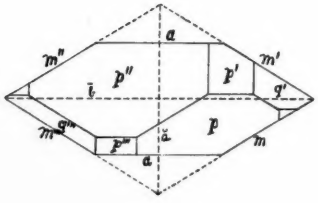

Fig. 2.

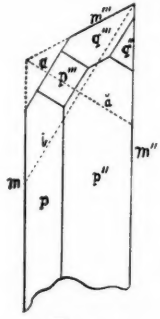

Fig. 3.

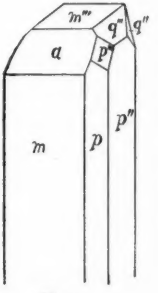

Fig. 4.

tained by allowing a hot saturated solution of the salt, contained in a platinum dish, to cool slowly over night. This was accomplished by placing the dish in a large tank of hot water and surrounding the latter with non-conducting material. The crystals obtained in this way were several millimeters in length and very

sharply defined. They were exceedingly brilliant and gave excellent reflections.

Orthorhombic.—Axes $\breve{a} : \bar{b} : \dot{c} = 0.6017 : 1 : 0.2799$.

		Measured.	Calculated.
mm‴,	$110 \wedge 1\bar{1}0 =$	*62° 4′	
mp,	$110 \wedge 111 =$	*61° 30′	
pp″,	$111 \wedge \bar{1}11 =$	*57°	
pp′,	$111 \wedge 1\bar{1}1 =$	48° 12′	48° 16′
pp‴,	$111 \wedge 11\bar{1} =$	28° 33′	28° 29′
ap,	$100 \wedge 111 =$	65° 52′	65° 52′
m‴p,	$1\bar{1}0 \wedge 111 =$	77°	77° 5′
mq,	$110 \wedge 131 =$	53° 8′	53° 8½′
qp′,	$131 \wedge \bar{1}11 =$	49° 48′	49° 46½′
qp,	$131 \wedge 111 =$	22° 56½′	22° 59′
qq′,	$131 \wedge 1\bar{3}1 =$	39° 13′	39° 13′

$2NaF.TaF_5.H_2O$.—This salt was studied by Marignac. It may be obtained in the form of thin plates when a solution containing sodium fluoride and a rather large excess of tantalum fluoride is concentrated and allowed to cool. On recrystallization, it passed into the 3 : 1 salt just described. Its analysis was conducted as in the case of the lithium salt.

	Calculated for $2NaF.TaF_5H_2O$.		Found. I.	Marignac.		
2NaF	84	22.11	22.15	22.40	22.51	22.17
TaF_5	278	73.17	72.94	72.49	72.74	73.02
H_2O	18	4.74	4.82	4.95	4.63	.....
	380	100.00	99.91	99.84	99.88	

$NaF.TaF_5$.—The mother-liquor from the 2 : 1 salt contained a large amount of tantalum fluoride, with only a small amount of sodium fluoride. From this solution there separated, after it had stood undisturbed for several weeks, a salt consisting of shining cubes belonging to the isometric system. While this salt was obtained only in small amount, the results seem to be sufficient to establish the existence of this ratio. It must be remembered that the highest purity cannot be expected in the case of double salts which are only formed in the presence of a large excess of one of the constituents and which cannot be purified by recrystallization.

		Calculated for $NaF.TaF_5$.	Found.
NaF	42	13.12	13.58
TaF_5	278	86.88	86.27
	320	100.00	99.85

POTASSIUM SALTS.

$2KF.TaF_5$.—This is the most important double fluoride of tantalum. From it, pure tantalic acid is obtained. By means of it, tantalum is separated from columbium. It was studied by Berzelius, H. Rose and Marignac. It is formed when the two fluorides are brought together in a dilute aqueous solution of hydrofluoric acid, and consists of small, but well-defined, anhydrous needles. On preservation it slowly gives off hydrofluoric acid, indicated by the etching of glass bottles containing the dry salt. For this reason neither this nor any of the other double fluorides were preserved in glass, but rather in clean pasteboard boxes. This salt was found to be much more soluble in hot than in cold water. Its solubility in the latter is given by Marignac to be 1 : 200 parts of water containing a small amount of hydrofluoric acid. Its solubility in pure water could not be determined as an insoluble oxyfluoride separates from the solution. This latter compound was also formed when a solution of potassium tantalum fluoride was boiled, provided that only a very small amount of free hydrofluoric acid was present. According to the analyses made by Marignac this white precipitate approached the composition indicated by the formula, $Ta_2O_5+2(2KF.TaF_5)$. This body was quite insoluble in water, but dissolved readily in hydrofluoric acid, and from the solution so obtained, the normal double fluoride again separated. On heating the dry normal salt in a platinum crucible it decrepitated and then fused to a clear colorless liquid.

The following analyses are given by the above-named investigators.

		Calculated for $2KF.TaF_5$.	Found.		
			Berzelius.	H. Rose.	Marignac.
2K	78	19.80	19.54	20.60	19.85
Ta	183	Ta_2O_5, 56.60	56.99	53.18	56.59
7F	133	33.79			33.42
	394				

Marignac employed this salt for the determination of the atomic weight of tantalum. The results of his analyses are given in the first two columns, while the third shows the atomic weight of tantalum calculated on the basis of O = 16, K = 39.15 and S = 32.06.

Ta_2O_5. Per cent.	K_2SO_4. Per cent.	At. wt. of Ta.
56.50	44.37	182.03
56.75	44.35	183.11
56.55	44.22	182.98
56.56	44.24	182.92

$2KF.TaO_2F_3.H_2O$.—This salt has already been prepared by A. Piccini. During the present investigation it was obtained by dissolving potassium tantalum fluoride in a hot, dilute, aqueous solution of hydrofluoric acid, and adding an equal volume of a 3 per cent. solution of hydrogen peroxide. On cooling, pearly leaflets separated from the liquid. They closely resembled in appearance the crystals of potassium columbium oxyfluoride. They were again crystallized from water containing some hydrogen peroxide and hydrofluoric acid. They were much more soluble than the normal potassium tantalum fluoride, and ammonium hydroxide did not precipitate the tantalum from their solution. On the other hand, precipitation took place at once in solutions of the normal salt. The addition of a small amount of alcohol along with the ammonium hydroxide produced a precipitate of tantalum hydroxide. The water was driven out of the salt at a much lower temperature than the active oxygen. This fact led Piccini to write the formula of the salt as indicated above.

Analysis.—One portion of the salt was dissolved in water in a platinum dish, boiled with a little alcohol and ammonium hydroxide, and the tantalum hydroxide produced was filtered out and washed. The filtrate was boiled with sodium carbonate to expel ammonia and the fluorine was then determined in the usual way as calcium fluoride.

The active oxygen and water were determined by weighing out a sample in a short hard glass tube closed at one end. A plug of asbestos was placed in the tube above the salt to prevent loss by decrepitation, and the tube was then connected to the top of a Hempel's gas burette by means of a short piece of rubber tubing. On gently heating the tube, water was expelled at first, and then at a higher temperature oxygen was evolved, and from its corrected volume the amount of active oxygen in the salt was easily calculated. The tube was then reweighed and its loss in weight gave the sum of the active oxygen and water, the latter being finally determined by difference.

The tantalum and potassium were determined as in the case of the other double fluorides.

	Calculated for $2KF.TaO_2F_3.H_2O$.		Found. I.	Found. Piccini.	
2K	78	19.21	19.56		18.83
Ta	183	45.07	44.87	44.28	44.82
5F	95	23.40	23.76		23.82
O (active)	16	3.94	3.96		3.78
H_2O	18	4.44	4.24	4.34	4.25
O	16	3.94	3.61 (Diff.)		
	406	100.00	100.00		

RUBIDIUM SALT.

$2RbF.TaF_5$.—This salt was obtained in very small amounts by Pennington. It was formed when the two fluorides were brought together in dilute aqueous hydrofluoric acid and consisted of small white needles. It was recrystallized from water containing a small amount of acid, but not from pure water, as a white, insoluble salt separated as in the case of the potassium salt. It was much more soluble than the latter, 1 part of the salt dissolving in about 40 parts of water. The following analytical results were obtained:

	Calculated for $2RbFTaF_5$.		Found. I.	Found. II.	Found. III.
2RbF	209	42.91	43.26		42.90
TaF_5	278	57.09	57.05	57.01	56.93
	478	100.00	100.31		99.83

On recrystallizing this salt several times from strong hydrofluoric acid a granular salt was obtained which gave 50 per cent. of Ta_2O_5 on analysis. This approaches the formula $3RbF.2TaF_5$, which requires 51.3 per cent. of Ta_2O_5, but repeated efforts to get a pure salt were without success. The results, however, seemed to point to the existence of a double fluoride richer in tantalum fluoride than the 2 : 1 salt.

SALTS OF CAESIUM.

Tantalum fluoride forms two different double fluorides with caesium fluoride. To prepare these salts pure caesium fluoride was obtained after the following manner: Commercial caesium carbonate was converted into caesium nitrate by solution in nitric acid. The solution was evaporated to dryness to expel the excess

of acid, and the salt was then dissolved in 1:1 hydrochloric acid and treated with the equivalent amount of iodine. On cooling the salt $CsCl_2I$, described by H. L. Wells,[1] crystallized out. This salt was recrystallized from 1:1 hydrochloric acid, and when tested by means of the spectroscope was found to be free from all other alkali metals. On careful ignition this trihalide gave pure caesium chloride, which was converted into the carbonate by the method of J. L. Smith,[2] which consists in a conversion of the chloride to nitrate by evaporation with nitric acid, and the evaporation of the caesium nitrate solution with pure oxalic acid and ignition of the dry residue. The hydrofluoric acid solution of this carbonate gave, on concentration, clear colorless prismatic crystals, and was used for the preparation of the following salts:

$CsF.TaF_5$.—This salt is the most definite and characteristic double fluoride of caesium and tantalum. It may be best prepared by bringing together solutions of the two fluorides in the calculated proportions, and recrystallizing from a rather strong solution of hydrofluoric acid. Brilliant, glistening rhombohedral crystals were formed. They were recrystallized unchanged from water containing hydrofluoric acid. This salt was also obtained when the 2:1 salt was crystallized two or three times from concentrated hydrofluoric acid, or when a mixture of caesium fluoride with a large excess of tantalum fluoride was allowed to crystallize.

The first two analyses are for a salt recrystallized from strong hydrofluoric acid, while the third analysis gives the results obtained for a salt crystallized in the presence of a large excess of tantalum fluoride.

		Calculated for $CsF.TaF_5$.	Found.		
			I.	II.	III.
		Per cent.	Per cent.	Per cent.	Per cent.
CsF	152	35.35	35.37	35.31	35.19
TaF_5	278	64.65	64.59	64.22	64.43
	430	100.00	99.96	99.53	99.62

Crystallography.—As stated above, this salt crystallized in the rhombohedral division of the hexagonal system. Many of the crystals showed faces of the right and left rhombohedron together with those of a hexagonal prism of the second order, as in the figure. At times the eight faces of one zone grew to a considerable

[1] *Amer. Jour. Sci.*, **43**, 17 (1892).
[2] *Ibid.*, II, **16**, 373.

length, giving the crystal a marked prismatic aspect. The faces of the crystals were smooth and brilliant, and gave very sharp

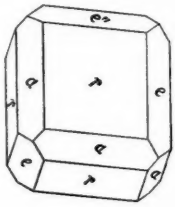

Fig. 5.

reflections. The measurements given represent the mean of a number of very concordant observations.

Rhombohedral.—Axis $\dot{c} = 1.0467$.

		Measured.	Calculated
rr′,	$10\bar{1}1 \wedge \bar{1}101 =$	83° 42⅔′	
ee′,	$01\bar{1}2 \wedge \bar{1}012 =$	53° 13′	53° 13′
ae,	$11\bar{2}0 \wedge 01\bar{1}2 =$	63° 23½′	63° 23½′
aa′,	$11\bar{2}0 \wedge \bar{1}2\bar{1}0 =$	60°	60°

$2CsF.TaF_5$.—This salt was obtained when tantalum fluoride and an excess of caesium fluoride were brought together and allowed to crystallize from a solution containing a slight amount of hydrofluoric acid. It consisted of small needles, and was much more soluble than the corresponding potassium salt. It could not be crystallized from water as it tended to pass into the 1 : 1 salt.

Analysis.—Caesium sulphate was found to be distinctly volatile at a red heat, so that care had to be exercised in its ignition. In order to convert all of the acid sulphate into the normal sulphate the mass was ignited with ammonium carbonate, this being repeated until the crucible had reached a constant weight. This same precaution was used in the ignition of rubidium sulphate, which was also somewhat volatile at elevated temperatures.

	Calculated for $2CsF.TaF_5$.		Found. I.	Found. II.
2CsF	304	52.23	51.95	52.03
TaF_5	278	47.77	47.40	47.52
	582	100.00	99.35	99.55

PYRIDINE SALTS.

$3(C_5H_5N.HF).2TaF_5.2H_2O$.—This salt was formed when a mixture of pyridine hydrofluoride and tantalum fluoride, in a slightly

acid solution, was concentrated on the water-bath and allowed to cool. The salt, much more soluble in hot than in cold water, was easily recrystallized from water containing a trace of hydrofluoric acid. When dry, it smelled quite strongly of pyridine. On standing in contact with the air the crystals soon lost their luster, becoming white and opaque. The freshly prepared crystals were soluble in water, methyl and ethyl alcohols, pyridine and hot nitrobenzene, but not in benzene.

Analysis.—The tantalum was obtained by igniting a sample of the salt with sulphuric acid. The carbon and hydrogen were determined by combustion, the sample being mixed with a large amount of lead chromate. The nitrogen was determined by the method of Dumas. The fluorine was determined in two ways: first, as calcium fluoride after the removal of the tantalum with ammonium hydroxide; second, by titration, using litmus as an indicator. At first an excess of the alkali was run into the solution of the salt contained in a platinum dish and boiled until all of the pyridine had been expelled. The solution was then made acid and titrated back with the standard alkali. The end-point was not as sharp as could be desired, but the results obtained were fairly satisfactory.

	Calculated for $3(C_5H_5N.HF).2TaF_5.2H_2O$.		Found. I.	Found. II.
2Ta	366	41.17	41.23	41.39
15C	180	20.25	20.43	20.16
22H	22	2.47	2.17	2.24
3N	42	4.72	4.77	4.75
13F	247	27.78	27.55	27.43
2O	32	3.60	3.85 (Diff.)	4.03 (Diff.)
	889	100.00	100.00	100.00

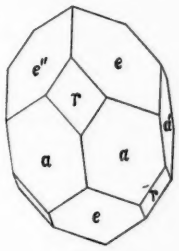

Fig. 6.

Crystallography.—This salt crystallized in the hexagonal system and had very much the same habit as the 1:1 caesium salt. The crystals were easily obtained by allowing the solution to evaporate spontaneously. They grew at times to a diameter of 10 mm. or more. Their faces gave fair images of the signal when measured with the goniometer. The crystal habit is shown in Fig. 6.

Rhombohedral.—Axis $\dot{c} = 1.6259$.

		Measured.	Calculated.
rr′,	$10\bar{1}1 / \bar{1}101 =$	99° 42′	
ra′,	$10\bar{1}1 / \bar{1}2\bar{1}0 =$	90°	90°
aa′,	$11\bar{2}0 / \bar{1}2\bar{1}0 =$	60°	60°
ee′,	$01\bar{1}2 / \bar{1}012 =$	72° 41′	72° 42′
ae,	$11\bar{2}0 / 01\bar{1}2 =$	53° 39½′	53° 39′
re′,	$10\bar{1}1 / \bar{1}012 =$	105° 6½′	105° 9′

$C_5H_5N.HF.TaF_5$.—It was found that when the preceding salt was recrystallized from strong hydrofluoric acid a new salt separated in the form of long slender needles. These needles were recrystallized from strong hydrofluoric acid and gave the following results on analysis:

	Calculated for $C_5H_5N.HF.TaF_5$.	Found.
Ta_2O_5	59.16	58.98
F	30.24	30.02
N	3.71	4.03

Crystalline salts were also obtained with methylamine, ethylamine, triethylamine and quinoline, but their analyses were not completed. There is little doubt but that a large number of such compounds can be obtained, and the subject will receive further attention.

AMMONIUM SALTS.

The investigation of the ammonium salts was not completed, but enough was accomplished to prove that other ratios than the 2:1 salt exist. For example, on concentrating a solution containing tantalum fluoride and an excess of ammonium fluoride a salt was obtained, 0.6035 gram of which gave 0.3450 gram of Ta_2O_5, or 57.17 per cent. That required for $3NH_4F.TaF_5$ is 57.33 per cent. These salts will receive further attention. The 2:1 salt was studied by Marignac and it was used by him in a determination of the atomic weight of tantalum. He obtained the following results, and from them the atomic weight of tantalum has been calculated, using H = 1.008, N = 14.04 and F = 19.

$2NH_4F.TaF_5$.	Ta_2O_5.	Per cent. Ta_2O_5.	At. wt. of Ta.
0.986	0.622	63.08	180.64
2.133	1.349	63.24	182.16
2.012	1.273	63.27	182.45
2.007	1.273	63.42	183.89

The great solubility of this salt precludes its use in accurate atomic weight determinations, as one could scarcely hope to obtain a perfectly pure and definite compound. In fact, the tendency of all these double fluorides to form more than one ratio presents an objection to their use as material for atomic weight determinations. Of the salts mentioned in this paper, the 2:1 potassium and the 3:1 sodium are by far the most desirable for such a purpose, as they may be obtained in a high state of purity by repeated crystallizations. However, other compounds of tantalum should be sought with which to accurately determine this constant.

PERTANTALATES.

While testing tantalum hydroxide it was noticed that it dissolved readily in an alkaline solution of hydrogen peroxide. In one instance tantalum hydroxide, which had been prepared by precipitating a solution of ammonium tantalum fluoride with ammonium hydroxide and washing the precipitate with water, was dissolved in a dilute solution of hydrogen peroxide containing some potassium hydroxide, and, on standing over night, a crystalline salt separated, which proved to be potassium pertantalate. This seemed to be a very convenient method for the preparation of the alkaline pertantalates, and it was therefore carried out on a larger scale.

A number of the salts of pertantalic acid have been described by P. Melikoff and L. Pissarjewsky.[1] Among others, they obtained the following:

$$K_3TaO_8 + \tfrac{1}{2}H_2O$$
$$Na_3TaO_8 + H_2O$$
$$CaKTaO_8 + 4\tfrac{1}{2}H_2O$$

The sodium and potassium salts were obtained as white precipitates upon the addition of alcohol to a dilute hydrogen peroxide solution of the corresponding tantalate. The third salt mentioned above was obtained from the potassium salt by double decomposition with calcium chloride.

[1] *Z. anorg. Chem.*, **20**, 340 (1899).

Potassium Pertantalate, K_3TaO_8.

Twenty grams of stick potassium hydroxide were dissolved in about 250 cc. of a 3 per cent. solution of hydrogen peroxide, and to this solution tantalum hydroxide, prepared as indicated above, was added as long as solution took place. The solution was then filtered and allowed to stand in a cool place over night. The anhydrous potassium pertantalate separated in small hard crystals nearly white in color. This salt was stable at the ordinary temperature. It dissolved slowly in water, and oxygen was evolved when its aqueous solution was boiled. The dry salt decomposed violently when treated with concentrated sulphuric acid.

Analysis.—A sample of the salt was dissolved in water, a few drops of sulphuric acid added and the solution boiled. The tantalum separated as the hydroxide, which was filtered off and weighed. The filtrate was evaporated and the potassium determined as sulphate.

The active oxygen in this salt was determined as outlined under the potassium salts.

The analyses given are for two separate preparations.

	Calculated for K_3TaO_8.		Found.	
		Per cent.	I. Per cent.	II. Per cent.
$\frac{1}{2}Ta_2O_5$	223	52.04	52.01	51.78
$1\frac{1}{2}K_2O$	141.5	33.02	32.83	32.99
4O (active)	64	14.94	14.92	14.97
	428.5	100.00	99.76	99.74

Sodium Pertantalate, $Na_3TaO_8+14H_2O$.

This salt was prepared in the same manner as the potassium salt. It crystallized from the solution in large, but not well-defined, crystals, which had a faint yellow color. On exposure to the air these crystals rapidly lost the greater part of their water of crystallization, falling to a white powder. For analysis the crystals were dried between folds of filter-paper and weighed out as rapidly as possible.

	Calculated for $Na_3TaO_8+14H_2O$.		Found.
$\frac{1}{2}Ta_2O_5$	223	35.28	35.34
$1\frac{1}{2}Na_2O$	93	14.72	15.14
4O (active)	64	10.13	10.09
$14H_2O$	252	39.87	38.89
	632	100.00	99.46

On adding the chlorides of calcium, strontium or barium to solutions of the above-described pertantalates, flocculent precipitates were produced. These compounds will receive further attention.

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A CONTRIBUTION TO THE CHEMISTRY OF THE TELLURATES.[1]

BY EDGAR BURTON HUTCHINS, JR.

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THIS work was undertaken with a view of preparing a number of the tellurates and studying their properties. The work has been confined for the most part to the salts of potassium, silver, and mercury. Careful attention has been devoted to their preparation in the crystalline form. The ease with which the tellurates of silver and mercury are decomposed by water has made this problem particularly difficult. For the most part the salts appear at first as amorphous precipitates of varying composition and quickly alter in the mother-liquor, their subsequent composition depending on the conditions in the solution.

The telluric acid used in this work was obtained by purifying and oxidizing electrolytic tellurium prepared by the Baltimore Copper Co. This tellurium contains silver, copper, and selenium as its principal impurities. The acid was prepared by the method described by Staudenmaier.[2] By this method free telluric acid is obtained by oxidation of tellurous acid by means of chromic acid. In many respects this method is superior to those in which sulphuric acid is used to set the telluric acid free. The yield is greater, the operation is more direct, and the sulphuric and selenic acids are eliminated in one of the first steps of the process which consists in purifying tellurium dioxide. These acids are apt to contaminate telluric acid prepared by the other methods, unless special precautions are taken.

The method as carried out in this work is as follows:

Tellurium is dissolved in aqua regia and the resulting solution freed from nitric acid by evaporating with excess of hydrochloric acid. After the hydrochloric acid solution has been diluted and

[1] From a thesis submitted for the degree of Doctor of Philosophy, University of Wisconsin, 1905.

[2] *Z. anorg. Chem.*, **10**, 189.

filtered, the tellurium is precipitated by means of sodium acid sulphite and repeatedly washed with hot water. The moist tellurium is oxidized with nitric acid and the resulting basic nitrate purified by recrystallization.

The purified basic nitrate is covered with several times its bulk of dilute nitric acid. A little more chromic acid is added to the solution than is required by the equation $3TeO_2 + 2CrO_3 + 3H_2O = 3H_2TeO_4 + Cr_2O_3$. When the mixture is boiled for some time the tellurium dioxide is completely oxidized to telluric acid according to the above equation. The solution is then concentrated over the water-bath until a crystalline crust begins to form and allowed to cool slowly. The solution is cooled, decanted, and again concentrated over the water-bath until crystals form. This operation is repeated as long as telluric acid separates from the mother-liquor.

The telluric acid, which is green from the presence of chromium nitrate, is dissolved in hot water and recrystallized. If a white residue remains when the acid is dissolved, it is an indication that the amount of chromic acid was insufficient to oxidize all of the tellurium dioxide. A residue may remain even when the hot nitric acid solution is clear. This is due to the fact that tellurium dioxide is much more soluble in hot nitric acid than in cold, and so may separate with the telluric acid when the solution is cooled. In order to remove the chromium nitrate from the telluric acid and obtain a pure white product the acid must be recrystallized from ten to twenty-five times, depending upon the amount of the chromium salt present.

It has been found possible to prepare 1500 grams of the recrystallized acid in six weeks. The yield is about 80 per cent. Telluric acid remains in the mother-liquor along with the chromium nitrate, from which it cannot be readily separated as the solution becomes syrupy upon evaporation.

Telluric acid is a weak acid, showing but a feeble reaction to litmus. Gutbier[1] found that telluric acid has about the same molecular conductivity as hydrocyanic acid or hydrogen sulphide. He determined the molecular weight of telluric acid by the freezing-point method. From the results which he obtained he concludes that telluric acid should be represented by the formula $Te(OH)_6$ and not $H_2TeO_4 + 2H_2O$.

[1] "Studien über das Tellur," p. 16.

When heated above 110° telluric acid loses water. According to Gutbier constant weight is obtained at 145°. He shows that the loss in weight at that temperature is not as great as that required by the change of $H_2TeO_4.2H_2O$ to H_2TeO_4. Experiments carried out during the progress of this work have given results similar to those obtained by Gutbier.

Mylius[1] stated that $H_2TeO_4.2H_2O$ is changed to $(H_2TeO_4)_n$ at about 140°. He called the polymerized acid allotelluric acid and showed that its solutions have a much greater conductivity than the acid that has not been dehydrated. The conductivity of solutions of allotelluric acid, according to Mylius, diminishes upon standing. This may indicate that the acid gradually assumes the composition H_6TeO_6 when in solution.

While telluric acid may be considered a weak acid, a hot aqueous solution of it will attack many metals such as silver, mercury, lead, bismuth, copper, zinc, arsenic, antimony, tin, aluminum, cadmium, and nickel. A number of these metals are attacked by a cold solution of the acid.

SALTS OF TELLURIC ACID.

The types of salts that telluric acid forms may be represented as follows: $(2M_2O.3TeO_3)$, $(M'_2O.2TeO_3)$, $(M'_2O.TeO_3)$, $(3M'_2O.2TeO_3)$, and $(3M'_2O.TeO_3)$. Crystalline salts of all of these types are now known. With the possible exception of mercuric orthotellurate[2] (Hg_3TeO_6) no anhydrous crystalline salt has been described. It is claimed by Nandl and von Lang[3] that K_2TeO_4 exists as a crystalline salt in the anhydrous condition, but its existence has been disputed[4] by Retgers, Rammelsberg, Staudenmaier, and Gutbier.

Berzelius considered telluric acid a dibasic acid and accordingly called salts of the type M'_2TeO_4 normal tellurates and salts of the other types basic or acid tellurates, according as they contain more or less metallic oxide than the normal salt. This nomenclature has been universally adopted in describing the tellurates and is adhered to in the following description. However, salts of the type M'_6TeO_6 are termed orthotellurates from their evident relation to orthotelluric acid, H_6TeO_6.

We have both amorphous and crystalline salts of the type

[1] *Ber.*, **34**, 2208.
[2] New salt.
[3] *Wiener Akad. Ber.*, **43**, 117.
[4] Gutbier: "Studien über das Tellur," p. 36.

M'_6TeO_6 such as Ag_6TeO_6,[1] Hg''_3TeO_6,[2] Cu_3TeO_6,[3] and $Zn_3\ TeO_6$.[3] These salts appear to be derived from the acid H_6TeO_6 which is identical in composition with ordinary telluric acid.

The crystalline salts of the type $M_2O.TeO_3$ contain two or more molecules of water; for example, $(Na_2O.TeO_3.2H_2O)$,[4] $(K_2O.TeO_3.2H_2O)$,[5] $(Cs_2O.TeO_3.3H_2O)$,[6] $(Rb_2O.TeO_3.3H_2O$,[6] $(Ag_2O.TeO_3.2H_2O)$,[2] $(HgO.TeO_3.2H_2O$.[2] These compounds may be considered acid salts of orthotelluric acid of the types—$(Na_2H_4TeO_6)$, $(K_2H_4TeO_6)$, $(Cs_2H_4TeO_6.H_2O)$, $(Ag_2H_4TeO_6)$, (HgH_4TeO_6).

Likewise the silver salt $(3Ag_2O.2TeO_3.3H_2O)$, which according to the nomenclature in vogue is a basic salt, may be considered an acid salt of the type $Ag_3H_3TeO_6$.

This view of the tellurates finds some confirmation in the experiments of Gutbier and Mylius on the molecular weight and electrical conductivity of telluric acid. It is also supported by the behavior of the hydrous tellurates when heated. Gutbier[7] has shown that the alkali tellurates decompose with the liberation of oxygen before the water which they contain is entirely driven off. The silver salts mentioned do not give up all of their water until a temperature of 200° is reached. Oxygen is evolved from these salts at a temperature only a few degrees above this point.

Some of the crystalline tellurates contain more water than is required to make them derivatives of orthotelluric acid; such salts are $K_2TeO_4.5H_2O$[8] and $HHgTeO_4.3H_2O$.[9] These compounds may be considered acid salts containing water of crystallization, thus,—$K_2H_4TeO_6.3H_2O$ and $HgH_5TeO_6.H_2O$.

Such crystalline salts as $CsHTeO_4.\frac{1}{2}H_2O$ and $RbHTeO_4.\frac{1}{2}H_2O$[10] would have to be considered salts of a higher acid, as $H_6Te_2O_9$.

Corresponding to the type M'_2TeO_4 a large number of anhydrous tellurates have been prepared but they are all amorphous. These salts may also be considered metatellurates. Their relation to orthotelluric acid is similar to that which the metaborates

[1] Amorphous, Berzelius.
[2] Crystalline, new salt.
[3] Amorphous, new salts.
[4] Berzelius.
[5] Retgers: *Z. phys. Chem.*, **10**, 536.
[6] Norris and Kingman: *Am. Chem. J.*, **26**, 320.
[7] "Studien über das Tellur.," p. 34.
[8] Berzelius.
[9] New salt.
[10] Norris and Kingman: *Loc. cit.*

bear to orthoboric acid. It is problematical how much water these salts would contain were it possible to prepare them in the crystalline condition.

In addition to the types of tellurates enumerated above a number of tellurates corresponding to $M_2Te_2O_7$ have been prepared. They have been called the pyrotellurates. Berzelius also described the salts $Na_2O.4TeO_3.5H_2O$ and $K_2O.4TeO_3.4H_2O$.

Methods of Analysis.

In the analysis of the tellurates of those metals whose chlorides are not volatile below a red heat the tellurium has been volatilized as $TeO_2.2HCl$ and the non-volatile chloride weighed. This method of determining the metal is preferred to the method of precipitation because it is less time-consuming; there are fewer operations required for the analysis and less opportunity for experimental error. In cases where it is applicable, that is, where the chloride of the metal is not readily volatile, it gives at once a clean separation of the metal from telluric acid. Moreover, the tellurium is obtained in a suitable solution for precipitation with sulphur dioxide.

Professor Lenher[1] has shown that when dry hydrochloric acid gas is passed over a tellurite heated to a temperature somewhat below redness the tellurium is completely volatilized as $TeO_2.2HCl$. If the chloride of the metal is not volatile it remains in the boat. He has employed this method in the analysis of a number of the tellurites. The method has been found to work equally well for the analysis of salts of telluric acid. Following is a description of the method as it has been carried out.

A sample of the tellurate to be analyzed is placed in a porcelain boat which has been weighed. The boat is loosely covered with a thin glass plate and introduced into a hard glass tube. Hydrochloric acid gas is generated by allowing concentrated hydrochloric acid to drop slowly into a flask containing concentrated sulphuric acid. In this manner a steady stream of the gas is provided. The gas after having been dried by sulphuric acid is passed through the tube, which is heated to a dull red heat. The hydrochloric acid decomposes the tellurate with the formation of the chloride of the metal, chlorine, and $TeO_2.2HCl$ according to the following equation: $M_2TeO_4+6HCl=2MCl+2Cl+TeO_2.2HCl+2H_2O$. The tellurium compound sublimes upon

[1] Unpublished notes.

the cold part of the tube in the form of crystalline flakes leaving only the chloride of the metal in the boat. The boat is removed from the tube, cooled in a desiccator and weighed. The escaping hydrochloric acid gas is collected in a receiver containing cold water. The tellurium may be washed from the tube into the receiver with hydrochloric acid and precipitated with sulphurous acid. Tellurium was repeatedly determined by this method.

The method which Norris and Kingman[1] used in the analysis of the tellurates was largely employed for the estimation of tellurium. This method depends upon the fact that hot aqueous hydrochloric acid completely reduces telluric acid to tellurium tetrachloride with the liberation of free chlorine, according to the following equation: $H_2TeO_4 + 6HCl = Cl_2 + TeCl_4 + 4H_2O$. This reaction goes on only slowly, if at all, in the cold. The analysis is carried out as follows:

The sample to be analyzed is placed in a small round-bottomed flask together with a small piece of magnesite. About 50 cc. of concentrated hydrochloric acid are added. The solution is heated until about one-third of it has distilled over, the distillate being collected in a solution of potassium iodide kept cool by a freezing-mixture. The liberated iodine is titrated with a solution of sodium thiosulphate.

To test the accuracy of this method a weighed amount of recrystallized telluric acid was decomposed by hydrochloric acid. The chlorine liberated by the reaction was absorbed by a solution of potassium iodide and the liberated iodine titrated with a solution of sodium thiosulphate. The solution of sodium thiosulphate was standardized against pure iodine. 0.4465 gram of telluric acid liberated chlorine equivalent to 0.2482 gram of tellurium. $H_2TeO_4.2H_2O$ requires 55.56 per cent. Te. Found, 55.59 per cent.[2]

If it is desired, the metal may be determined in the solution after the tellurate has been reduced and the chlorine distilled. This was done in some cases where the amount of material at hand was small.

Tellurium can be determined in telluric acid or its salts much more quickly by this method than by any method requiring precipitation of elementary tellurium. The entire determination

[1] *Loc. cit.*

[2] All calculations have been made on the basis of Te = 127.6.

requires less than one hour. Moreover the method has proven more reliable as carried out in this work than precipitation of elementary tellurium by sulphur dioxide.

In separating mercury from telluric acid use has been made of the fact that tellurium sulphide is soluble in a solution of ammonium sulphide. The tellurate of mercury is dissolved in dilute hydrochloric acid. Mercurous compounds are oxidized by chlorine or bromine water. If the acid solution is saturated with hydrogen sulphide in the cold only a trace of telluric acid is reduced.[1] The solution of telluric acid is then decanted from the precipitated mercuric sulphide. The precipitate is washed by decantation with hydrogen sulphide water to free it from telluric acid, and then digested with ammonium sulphide to remove the trace of tellurium precipitated with the mercuric sulphide.

Water was determined in most cases by heating the tellurate in a current of dry air and collecting the water in sulphuric acid.

THE TELLURATES OF SILVER.

Normal Silver Tellurate.

Berzelius[2] described normal silver tellurate (Ag_2TeO_4) as a dark yellow precipitate. He stated that he obtained this compound in the form of bulky flakes by adding a concentrated solution of silver nitrate to a solution of normal potassium tellurate.

It has not been found possible to prepare normal silver tellurate (Ag_2TeO_4) in pure condition by precipitation as described by Berzelius. When solutions of silver nitrate and normal potassium tellurate are brought together, the precipitate contains basic silver tellurate. The formation of a basic salt may be obviated by using an acid tellurate of potassium, for example, $KHTeO_4$, in place of the normal tellurate. But under these conditions the precipitate may contain an excess of telluric acid. Moreover when the precipitate is washed it is decomposed, forming a basic tellurate of silver.

It has been found possible to prepare well-crystallized normal silver tellurate. Crystals of this salt are not rapidly attacked by cold water and may be obtained free from basic salts.

Action of Telluric Acid on Oxide of Silver.

When silver oxide is treated with a slight excess of a solution

[1] Brauner: *J. Chem. Soc.* (London), **67**, 545.
[2] *Pogg. Ann.*, **32**, 577.

of telluric acid, normal silver tellurate is formed according to the equation: $Ag_2O + H_2TeO_4.2H_2O = Ag_2TeO_4.2H_2O + H_2O$.

The silver tellurate obtained by this method has quite different physical properties from the yellow precipitate described by Berzelius and Gutbier. It is a heavy granular powder nearly white in color. It has the composition $Ag_2TeO_4.2H_2O$. It is much more stable in the presence of water than the yellow precipitate hitherto described. When the powder is heated to 100° it loses a part of its water and assumes a brown color, but it does not give up all of its water until a much higher temperature is reached.

For analysis the salt was dried over sulphuric acid and dissolved in dilute nitric acid. The silver was precipitated from the solution by dilute hydrochloric acid. The filtrate was evaporated with an excess of hydrochloric acid to free it from nitric acid. The tellurium was precipitated in the hydrochloric acid solution by sulphurous acid.

Analysis gave the following results:

0.9597 gram gave 0.6172 gram AgCl and 0.2755 gram Te.

0.9051 gram gave 0.0724 gram H_2O.

Calculated for $Ag_2TeO_4.2H_2O$: Ag, 48.68; Te, 28.77; H_2O, 8.11. Found: Ag, 48.40; Te, 28.06; H_2O, 7.99.

Crystalline $Ag_2TeO_4.2H_2O$.

It has been found possible to obtain crystals of normal silver tellurate by slowly evaporating a solution made by bringing together dilute solutions of telluric acid and silver acetate containing free acetic acid. The dilute acetic acid holds the tellurate of silver in solution and allows it to crystallize as the solution is evaporated. The acetic acid solution must be quite dilute, as a strong solution of the acid prevents the formation of silver tellurate.

When solutions of silver acetate and telluric acid of moderate concentration are brought together, a lemon-yellow precipitate is formed. The precipitate closely approximates Ag_2TeO_4 in composition. When a solution of silver acetate containing 2.0 grams of silver acetate and a few drops of free acetic acid per liter, is mixed with an equal volume of a solution of telluric acid containing 1.4 grams of the acid per liter, no precipitate is formed. When such a solution is allowed to evaporate in the dark at room temperature, yellow crystals of $Ag_2TeO_4.2H_2O$ are formed. The

free telluric acid in the solution prevents the decomposition of the normal salt by the water. Only small amounts of the salt have been prepared in this manner. Larger quantities of the salt are more conveniently prepared as follows:

Upon adding an excess of a solution of silver nitrate to a concentrated solution of potassium tellurate containing a little free acetic acid a yellow or brown precipitate is formed. Analysis showed that this precipitate approximates normal silver tellurate in composition. Its exact composition depends largely on the concentration of the solution. It was observed that when such a solution is allowed to remain in contact with the precipitate for a few hours a heavy yellow salt separates at the bottom of the beaker. The salt is composed of distinct crystals of a straw-yellow color. As the crystals have a much higher specific gravity than the amorphous precipitate, they can easily be separated from it by elutriation. If the precipitate is allowed to remain in the mother-liquor for several days, red crystals of a basic silver tellurate will usually be found among the yellow crystals of the normal salt.

The crystalline normal salt may be prepared entirely free from basic silver tellurate by allowing the precipitate obtained by mixing solutions of silver nitrate and acid potassium tellurate to remain in the mother-liquor until it assumes the crystalline form.

Analysis of the yellow crystals gave the following results:

0.7638 gram gave 0.0605 gram H_2O.

0.4847 gram gave 0.3117 gram AgCl.

0.4980 gram, when heated with hydrochloric acid, gave sufficient chlorine gas to liberate 0.2828 gram of iodine from potassium iodide.

Calculated for $Ag_2TeO_4.2H_2O$: H_2O, 8.11; Ag, 48.68; Te, 28.77. Found: H_2O, 7.92; Ag, 48.41; Te, 28.57.

In this analysis the silver was precipitated with hydrochloric acid from a dilute nitric acid solution of the salt.

$Ag_2TeO_4.2H_2O$ crystallizes in the orthorhombic system. The crystals resemble those of sulphur both in the forms that occur and in the axial ratios. They are insoluble in hot or cold water but soluble in ammonia, potassium cyanide, sodium thiosulphate, and nitric, acetic, and sulphuric acids. Concentrated nitric, acetic, or sulphuric acids completely decompose silver tellurate, giving free telluric acid and the corresponding silver salt.

When crystals of the normal salt are allowed to remain for some time in contact with a cold solution of a silver salt, red crystals of the basic tellurate $3Ag_2O.2TeO_3.3H_2O$ are formed. The change is much more rapid in a 10 per cent. solution of silver nitrate at a temperature of 50° than in the cold. It takes place very slowly even in cold water.

Crystals of $Ag_2TeO_4.2H_2O$ darken slowly when exposed to the light. When the powdered crystals are compressed between steel rolls they detonate. When heated above 100° the crystals lose water and take on a brilliant purplish black lustre. They maintain this lustre until a temperature of about 200° is reached. As the temperature is raised still higher oxygen is evolved, the mass assumes a gray-brown color and fuses.

In order to determine whether silver sulphate and silver tellurate are isomorphous, crystals of $Ag_2TeO_4.2H_2O$ were introduced into a saturated solution of silver sulphate and the solution allowed to evaporate. Silver sulphate crystallized out of the solution entirely independent of the silver tellurate. Silver sulphate (Ag_2SO_4) and silver tellurate ($Ag_2TeO_4.2H_2O$) are therefore not isomorphous. It may be stated that the tellurate of silver was decomposed by the solution to some extent, a few red crystals of a basic tellurate being formed:

The sulphate and selenate of silver are isomorphous, their axial ratios being as follows:

Silver sulphate $a:b:c=0.5712:1:1.238$.

Silver selenate $a:b:c=0.5945:1:1.256$.

The axial ratios for silver tellurate were found to be:

$$a:b:c=0.722:1:2.107.$$

However, the sulphate and selenate cannot properly be compared with the tellurate of silver since they are anhydrous, while silver tellurate contains two molecules of water.

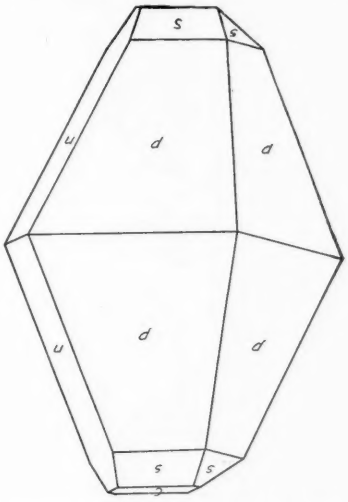
$Ag_2TeO_4.2H_2O$.

Orthorhombic. Axes—$a:b:c=0.722:1:2.107$.

pp''',	$111 : 1\bar{1}1$	$= 111° 26'$.
pp',	$111 : 111$	$= 77° 25'$.
cp,	$001 : 111$	$= 105° 40'$.
cn,	$001 : 011$	$= 115° 29'$.
cs,	$001 : 113$	$= 103° 02'$.

The crystals that were used for measurement were obtained by double decomposition of solutions of silver nitrate and potas-

sium tellurate containing a little free acetic or nitric acid. The amorphous precipitate that formed on mixing the solutions



slowly dissolved in the free acid, while at the same time crystals of $Ag_2TeO_4.2H_2O$ were formed upon the walls of the containing vessel.

In addition to the tellurate of silver described by Berzelius, Oppenheim[1] describes a crystalline precipitate, which he obtained in small quantity by adding a saturated solution of telluric acid to a concentrated solution of silver nitrate. He states that it differs from any tellurate of silver obtained by Berzelius in that it is crystalline and colorless. When exposed to the air it assumed a yellow color, according to Oppenheim. He states that he did not make a quantitative analysis of the substance, but concluded that it was a double compound of silver tellurate and nitrate, since he found that it contained nitric and telluric acids together with silver.

Gutbier[2] attempted to prepare the crystalline compound described by Oppenheim. When a concentrated solution of telluric acid is added to a concentrated solution of silver nitrate a red-

[1] *J. prakt. Chem.*, **71**, 256.
[2] *Loc. cit.*

brown or yellow precipitate is formed. This precipitate is the only product that Gutbier obtained from such solutions.

When a solution of silver nitrate is added to a dilute solution of telluric acid no precipitate is formed. But if the solutions are sufficiently concentrated and an excess of telluric acid added, a yellow flocculent precipitate is formed in small quantity. If the solution and precipitate are allowed to remain together in a dark place at room temperature for a few hours the amorphous precipitate changes to straw-yellow crystals of $Ag_2TeO_4.2H_2O$. This is the crystalline compound that Oppenheim obtained. Under the conditions of the experiment the crystals might easily be contaminated by silver nitrate.

Acid Tellurates of Silver.

Attempts were made to prepare the acid tellurates of silver described by Berzelius. It was not found possible to obtain precipitates having either the composition $AgHTeO_4$ or $Ag_2Te_4O_{13}$. The precipitates obtained in the manner described by Berzelius contain more telluric acid than is required by normal silver tellurate (Ag_2TeO_4), but upon remaining in the mother-liquor for some hours they are largely transformed to crystalline $Ag_2TeO_4.2H_2O$. It would hardly be expected that a solution of $KHTeO_4$ would yield $AgHTeO_4$ with silver nitrate, when it is known that telluric acid and silver nitrate give the crystalline normal tellurate.

Basic Silver Tellurates.

Berzelius[1] described two basic tellurates of silver, $3Ag_2O.2TeO_3$ and $3Ag_2O.TeO_3$, both of which were obtained as brown precipitates. He stated that boiling water decomposes the normal tellurate of silver into $3Ag_2O.2TeO_3$ and telluric acid.

$3Ag_2O.2TeO_3.3H_2O$.

In addition to the brown precipitates of $3Ag_2O.2TeO_3$ and $3Ag_2O.TeO_3$ already described, a crystalline tellurate of silver having the composition $3Ag_2O.2TeO_3.3H_2O$ was prepared during the progress of this work. When the precipitate obtained by the double decomposition of moderately dilute solutions of silver nitrate and potassium tellurate assumes the crystalline condition, both yellow crystals of $Ag_2TeO_4.2H_2O$ and red crystals of $3Ag_2O.2TeO_3.3H_2O$ are formed. The relative amounts of these salts obtained depends largely upon the temperature of the

[1] *Loc. cit.*

solutions and their concentration. When the solutions are cold and concentrated but little of the basic salt is formed. On the other hand, if the solutions are very dilute and warm, it is possible to obtain the crystalline basic tellurate free from the normal salt.

Analysis of the red crystals gave the following results:

0.2812 gram gave 0.0653 gram Te.

0.3763 gram gave 0.2917 gram AgCl.

1.6094 grams gave 0.0797 gram H_2O.

Calculated for $3Ag_2O.2TeO_3.3H_2O$: Te, 23.18; Ag, 58.83; H_2O, 4.90. Found: Te, 23.22; Ag, 58.35; H_2O, 4.95.

$3Ag_2O.2TeO_3.3H_2O$ crystallizes in ruby-red, transparent crystals belonging to the monoclinic system. The crystals remain unchanged in cold water. They are gradually decomposed by boiling water with the formation of a brown residue, probably $3Ag_2O.TeO_3$. In the sunlight the crystals become opaque and assume a copper color. When heated above 110° they lose water and become black, but all of the water is not given up until a temperature of about 200° is reached.

Just as it is possible to obtain crystals of hydrous normal silver tellurate by evaporation of solutions of silver tellurate under proper conditions, so it is possible by varying the conditions to obtain crystals of $3Ag_2O.2TeO_3.3H_2O$ directly from clear solutions. If a dilute solution of potassium tellurate is added to a large excess of silver nitrate containing a little free nitric acid, the solution filtered and allowed to evaporate at room temperature, red crystals of the basic salt are formed. The formation of crystals when the solution is evaporated is made possible by the fact that the dilute nitric acid is saturated with silver tellurate dissolved from the amorphous precipitate. If the solution contains much nitric acid the silver tellurate is entirely decomposed with the formation of silver nitrate and telluric acid so that no crystals of the tellurate of silver appear when the solution is evaporated. Consequently, a large volume of solution is necessary in order to obtain a small amount of the crystalline salt. Crystals of $3Ag_2O.2TeO_3.3H_2O$ have been repeatedly obtained in this manner, but only in small quantities.

Larger quantities of the salt have been prepared by double decomposition of solutions of silver nitrate and potassium tellurate, and subsequent change of the amorphous precipitate thus obtained

into the crystalline salt. If the solution contains no free acid the crystals form only in contact with the amorphous precipitate, since silver tellurate is insoluble in water. If, however, the solution contains a little free nitric or acetic acid, red crystals of $3Ag_2O.2TeO_3.3H_2O$ frequently form on the walls of the containing vessel.

THE TELLURATES OF POTASSIUM.

Normal Potassium Tellurate.

Berzelius[1] stated that normal potassium tellurate can be prepared by treating potassium carbonate with telluric acid. These compounds were dissolved together in equimolecular quantities and the solution evaporated to dryness. The residue was dissolved in water and the solution evaporated *in vacuo* over sulphuric acid until a crystalline crust formed. According to Berzelius this crust consisted of normal potassium tellurate. If the solution is evaporated at a moderate temperature a gummy mass is deposited.

Experiments were undertaken to ascertain whether normal potassium tellurate could be obtained by this method. It was found that solutions made by dissolving equivalent quantities of potassium carbonate and telluric acid in water always yield a gummy mass when they are evaporated *in vacuo*.

Potassium tellurate crystallizes from its solutions if they are allowed to evaporate very slowly. This separation of the crystalline salt is aided by the addition of a few crystals of the salt. When solutions, made according to the directions of Berzelius, are evaporated in this manner no crystals are formed. The gummy mass even separates around the crystals of $K_2TeO_4.5H_2O$, introduced into the solution. This pasty mass evolves carbon dioxide when treated with hydrochloric acid. The same result is obtained if the solution is cooled to zero instead of evaporated.

That all of the carbon dioxide appearing in the gummy mass had not been absorbed from the air is shown by the following experiment: 1.42 grams of anhydrous potassium carbonate and 2.37 grams of telluric acid were dissolved in a little water. The solution was at once evaporated to dryness over a free flame. The residue copiously evolved carbon dioxide when treated with hydrochloric acid. It is evident that telluric acid cannot replace all of the carbonic acid in an equimolecular quantity of potassium carbonate. This fact is in harmony with the fact, observed

[1] *Pogg. Ann.*, **32**, 579.

by Berzelius, that carbon dioxide reacts on normal potassium tellurate to form acid potassium tellurate, $KHTeO_4$, and potassium carbonate.

No carbon dioxide is evolved when saturated solutions of acid potassium tellurate ($KHTeO_4$) and potassium carbonate are brought together at 95° in the proportion of two molecules of the acid tellurate to one of the carbonate. $KHTeO_4$ is more soluble in a solution of potassium carbonate than in water.

$K_2TeO_4.5H_2O$.

Berzelius[1] prepared crystalline $K_2TeO_4.5H_2O$ from concentrated solutions of potassium hydroxide and telluric acid in the following manner: A solution of potassium hydroxide was added to a solution of telluric acid until a permanent precipitate formed, indicating the presence of an excess of the alkali. The gummy precipitate was dissolved by warming the solution. Crystals of $K_2TeO_4.5H_2O$ separated from the solution upon cooling it to zero.

$K_2TeO_4.5H_2O$ may be obtained in the form of crystals by slow evaporation of solutions of the salt at room temperatures. Whenever solutions of potassium tellurate are allowed to evaporate *in vacuo* over sulphuric acid they solidify to a gummy mass which does not become crystalline until it is dry. In order to bring about slower evaporation of the solution the loosely covered dish containing the solution may be placed in a desiccator over sulphuric acid. The desiccator should be filled with air freed from carbon dioxide to prevent the formation of potassium carbonate and acid potassium tellurate. Potassium tellurate has been repeatedly crystallized from its solutions in this manner. The solution may be concentrated rapidly until its specific gravity is about 1.2 and then crystallized by slow evaporation. The fact that potassium tellurate is very soluble renders it somewhat difficult to obtain a nicely crystallized product. Frequently the crystals form radiating clusters but in other cases the crystals are distinct. Solutions of potassium tellurate that have become supersaturated can frequently be made to crystallize by adding a few crystals of $K_2TeO_4.5H_2O$ and preventing further evaporation by closely covering the solution.

Crystals of $K_2TeO_4.5H_2O$ may be obtained by slow evaporation of the solution resulting from the double decomposition of

[1] *Loc. cit.*

equivalent quantities of normal silver tellurate and potassium bromide solution. This may be readily accomplished in the following manner. The potassium bromide and silver tellurate are thoroughly ground together, treated with a little warm water and again triturated. After standing for some time in an atmosphere free from carbon dioxide the solution is filtered and crystallized in the manner described above.

Analysis of crystals obtained in this manner gave the following results:

0.9742 gram gave 0.2420 gram H_2O.

0.9742 gram gave 0.4010 gram KCl.

0.2839 gram with hydrochloric acid liberated chlorine equivalent to 0.1001 gram Te.

	Calculated for $K_2TeO_4.5H_2O$.	Found.
Water	25.01	24.84
Potassium	21.76	21.60
Tellurium	35.45	35.26

Crystals of $K_2TeO_4.5H_2O$ are soft and crumble under a slight pressure. Solutions of the salt are alkaline to litmus and attack glass.

Solutions of potassium tellurate containing two molecules of free potassium hydroxide to one of the tellurate yield crystals of $K_2TeO_4.5H_2O$ when evaporated slowly. The yield is small on account of the free alkali in the solution. Solutions of this kind were evaporated in order to ascertain whether potassium tellurate would crystallize with two or five molecules of water under these conditions.

	Calculated for $K_2TeO_4.5H_2O$.	Found.
Water	25.01	25.15
Potassium	21.75	21.63
Tellurium	35.45	35.79

$K_2TeO_4.2H_2O$.

Retgers[1] described a second crystalline tellurate of potassium ($K_2TeO_4.2H_2O$) which he prepared by dissolving telluric acid in a concentrated boiling solution of potassium hydroxide and allowing the solution to cool slowly. He stated that crystals of $K_2TeO_4.2H_2O$ are isomorphous with those of $K_2OsO_4.2H_2O$.

This salt was obtained in the form of distinct crystals by dissolving telluric acid in a hot concentrated solution of potassium

[1] *Z. physik. Chem.*, **10**, 536.

hydroxide and allowing the solution to cool. The yield was very small.

Analysis of the salt, after having been washed with water at zero and dried for a day over calcium chloride, gave the following results:

1.4806 grams gave 0.1767 gram of water.

Calculated for $K_2TeO_4.2H_2O$, 11.47. Found, 11.93.

When the solution of potassium hydroxide, from which the crystals of $K_2TeO_4.2H_2O$ had been removed, was diluted, a copious amount of $K_2TeO_4.5H_2O$ separated as small crystals. This fact indicates that the formation of the dihydrate in the concentrated solution is due to the dehydrating effect of the strong alkali. It is also evident that $K_2TeO_4.5H_2O$ is less soluble in a dilute solution of potassium hydroxide than $K_2TeO_4.2H_2O$ is in a concentrated solution.

Acid Tellurates of Potassium.

Berzelius stated that potassium bitellurate ($KHTeO_4$) may be obtained from equivalent quantities of telluric acid and potassium carbonate, but that it is produced with greater certainty by dissolving potassium carbonate and telluric acid in a small amount of hot water in such proportions that there shall be two molecules of telluric acid present to one of potassium carbonate. When such a solution is cooled the bitellurate of potassium separates upon the walls of the containing vessel in granular tufts. The formula $K_2O.2TeO_3.4H_2O$ is assigned to the crystalline salt.

Berzelius stated that potassium quadrotellurate ($K_2O.4TeO_3$) can be obtained by the same method as the bitellurate. In the case of the quadrotellurate, however, telluric acid and potassium carbonate were dissolved in the proportion of four molecules of the former to one of the latter. The formula $K_2O.4TeO_3.4H_2O$ is assigned to the crystalline salt. Berzelius stated that these salts may also be obtained by treating a solution of normal potassium tellurate with the requisite amount of an acid (nitric or sulphuric) to withdraw potassium.

$KHTeO_4$.

A tellurate of potassium containing more telluric acid than $KHTeO_4$ cannot be obtained by the action of carbon dioxide on normal potassium tellurate. When carbon dioxide is passed into a concentrated solution of potassium tellurate a white precipitate of potassium bitellurate ($KHTeO_4$) is immediately formed. The

precipitate may settle as a gummy mass, but it becomes granular when cooled to zero. The composition of this precipitate is not changed by prolonged contact with carbon dioxide. $KHTeO_4$, obtained in this manner, was repeatedly covered with distilled water, cooled to zero, and treated with carbon dioxide.

Analysis of the residue, after having been dried with filter paper, gave the following results:

0.5428 gram with hydrochloric acid liberated chlorine equivalent to 0.2415 gram Te.

0.9906 gram gave 0.2511 gram KCl.

1.5444 gram gave 0.3492 gram H_2O.

Found: Te, 44.49; K, 13.30; H_2O, 22.62.

After deducting the water, some of which was evidently held mechanically, the values obtained for potassium and tellurium correspond closely with those required by the formula $K_2O.2TeO_3$. In another experiment 18 per cent. of water was obtained from a sample dried with filter-paper, while the same sample gave 13.2 per cent. of water after having been dried over phosphorus pentoxide for several days. The calculated value for water in $KHTeO_4.2H_2O$ is 16.8 and for $KHTeO_4.1\frac{1}{2}H_2O$ (or $K_2O.2TeO_3.4H_2O$) 13.9. The latter formula is the one assigned to the bitellurate by Berzelius.

Potassium bitellurate may be obtained in the form of a transparent crystalline crust by slow evaporation of its solutions. It is only sparingly soluble in water at 0°, but is readily soluble in boiling water. It is alkaline to litmus.

$$K_2O.3TeO_3.5H_2O.$$

When solutions made by dissolving potassium carbonate and telluric acid together in water in the proportion of one molecule of the carbonate to four of the acid are evaporated, a white granular precipitate of $K_2O.3TeO_3.5H_2O$ is deposited. Analysis of the salt, after having been dried for eleven days over phosphorus pentoxide, gave the following results:

1.6971 grams gave 0.2075 gram H_2O.

1.6971 grams gave 0.3495 gram KCl.

1.3340 grams gave (with HCl) chlorine equivalent to 0.7207 gram Te.

	Calculated for $K_2O.3TeO_3.5H_2O$.	Found.
Water	12.65	12.22
Potassium	11.01	11.06
Tellurium	53.83	54.02

The salt reacts alkaline to litmus. Like the bitellurate it is much more soluble in hot water than in cold.

This acid salt may be obtained by dissolving potassium carbonate and telluric acid together in the ratio of one molecule of potassium carbonate to three of telluric acid.

MERCUROUS TELLURATES.

Berzelius[1] described normal mercurous tellurate (Hg_2TeO_4) as a yellow-brown precipitate obtained by adding powdered mercurous nitrate to a solution of potassium tellurate. When a solution of mercurous nitrate is used instead of the powdered salt, the yellow-brown precipitate gradually changes to a pale yellow color. Berzelius stated that this change in color is probably due to the formation of the bitellurate of mercury ($HgHTeO_4$) brought about by the free acid in the solution of the mercury salt.

The precipitates obtained by double decomposition of solutions of mercurous nitrate and a soluble tellurate or telluric acid may vary in composition from $HHgTeO_4$ to $3HgO.2TeO_3$.

However, any precipitate of mercurous tellurate may be changed to crystals of $HHgTeO_4.3H_2O$ by treatment with a cold concentrated solution of telluric acid. This acid tellurate is not only the only crystalline mercurous tellurate that has been prepared, but it is the only mercurous tellurate of definite composition that has been obtained during the progress of this work.

Mercurous tellurate is a striking example of a salt of a weak acid and a weak base. Slight variations of the conditions under which a salt is placed may bring about a change in its composition, causing it to become either more acid or more basic. This, together with the fact that the salt is readily decomposed giving free mercury and mercuric tellurate, renders the preparation of the tellurates of monovalent mercury somewhat difficult.

$HHgTeO_4.3H_2O$.

This crystalline salt may be obtained either by double decomposition of solutions of mercurous nitrate and telluric acid or by the action of telluric acid upon mercurous oxide.

When mercurous oxide is treated with a cold concentrated solution of telluric acid it is slowly attacked and colorless crystals of $HHgTeO_4.3H_2O$ are formed. As the resulting crystals are mixed with the unattacked oxide, this is not a suitable method for the preparation of the salt in pure condition.

[1] *Pogg. Ann.*, **32**, 577.

Large amounts of the salt may be conveniently prepared by treating a solution of mercurous nitrate with telluric acid and subsequent change of the precipitate to the crystalline salt. When the solution of telluric acid is added to a solution of mercurous nitrate a bright yellow precipitate is formed. If a large excess of telluric acid is added, the yellow precipitate becomes nearly white and slowly changes to colorless crystals of $HHgTeO_4.3H_2O$. The presence of considerable free nitric acid in the solution aids greatly in the formation of crystals of the salt. Under these conditions crystals frequently form on the walls of the containing vessel.

Analysis of the colorless crystals gave the following results:

1.9265 grams gave 0.2717 gram H_2O.

0.8459 gram gave 0.4358 HgS.

1.2416 grams with hydrochloric acid liberated chlorine equivalent to 0.3501 gram Te.

	Calculated for $HHgTeO_4.3H_2O$.	Found.
Mercury	44.78	44.40
Tellurium	28.57	28.21
Water	14.11	14.11

For the estimation of the mercury, all of which was present in the mercurous condition, the salt was treated with dilute hydrochloric acid and the precipitated mercurous chloride oxidized with bromine water. The mercury was precipitated with hydrogen sulphide.

Tellurium was estimated by decomposing the salt with hydrochloric acid, absorbing the liberated chlorine in a solution of potassium iodide and titrating the free iodine with sodium thiosulphate. The chlorine absorbed by the solution of potassium iodide represents only a portion of the chlorine liberated by the oxidation of the hydrochloric acid. When the tellurate is treated with hydrochloric acid in the cold, mercurous chloride is precipitated. Upon heating the solution the chlorine formed by the oxidation of the hydrochloric acid converts the mercurous chloride into mercuric chloride. The amount of chlorine thus reduced was calculated and added to the amount absorbed by the iodide solution in order to determine the amount of tellurium in the salt. The reactions involved may be represented as follows:

$$2HHgTeO_4 + 2HCl = Hg_2Cl_2 + 2H_2TeO_4 + H_2O.$$

$2H_2TeO_4 + 12HCl = 2TeCl_4 + 8H_2O + 2Cl_2$.

$Hg_2Cl_2 + Cl_2 = 2HgCl_2$.

One-half of the chlorine liberated during the reaction is reduced by the mercurous chloride in the solution.

$HgHTeO_4.3H_2O$ crystallizes in the triclinic system. It is insoluble in water but soluble in dilute acetic or nitric acid. Ammonium hydroxide reacts with the salt to form a black precipitate. Sunlight blackens the salt, but it is stable in the air if protected from the light. Crystals of the salt have been preserved in closed tubes for a year without losing their transparency or changing in any respect. With boiling water the crystals quickly decompose, telluric acid and a yellow amorphous tellurate being formed. An excess of cold concentrated mercurous nitrate solution brings about the same result. If the yellow basic precipitate is treated with an excess of telluric acid it may be changed to crystals of $HHgTeO_4.3H_2O$. When strongly compressed between steel rolls the salt detonates and assumes a brown color. The amorphous mercurous tellurates possess the same property. It has been observed that when a glass rod is drawn over the wet precipitate obtained by bringing together solutions of mercurous nitrate and potassium tellurate, it changes from a yellow to a brown color. The same change may be brought about by pressing the precipitate between layers of filter-paper.

Other Mercurous Tellurates.

All attempts to prepare normal mercurous tellurate in the crystalline form have been unsuccessful. Indeed, it has not been found possible to obtain an amorphous tellurate of mercury having exactly the composition Hg_2TeO_4. The salt is likely to be contaminated by either a basic or an acid tellurate of mercury, depending upon the conditions in the solution. The preparation of the salt is still further complicated by the fact that the precipitate obtained by double decomposition of mercurous nitrate and potassium tellurate contains nitric acid which it is difficult to remove by washing. Moreover, long-continued treatment with water decomposes the precipitate.

When a large excess of a cold concentrated solution of potassium tellurate is added to a concentrated solution of mercurous nitrate the yellow precipitate, which is first formed, quickly changes to a brown. The precipitate is slimy and difficult to wash. It approximates Hg_2TeO_4 in composition.

Impure $3Hg_2O.2TeO_3$ may be obtained as a yellow amorphous precipitate by treating a hot dilute solution of potassium tellurate with an excess of mercurous nitrate solution and washing the precipitate with hot water. It is hardly possible to obtain the precipitate free from nitric acid.

A mercurous tellurate analogous to silver orthotellurate (Ag_6TeO_6) has not been prepared. When the bulky yellow precipitate, obtained by treating a hot dilute solution of potassium tellurate with an excess of mercurous nitrate solution is washed with hot water and boiled for some time in water it is decomposed, giving free mercury. The precipitate may be boiled for several hours without changing in appearance, but at length it settles as a heavy, brown granular powder containing free mercury. This change may be hastened by rubbing some of the precipitate against the side of the beaker with a glass rod.

When the brown powder is heated with hydrochloric acid, elementary tellurium is precipitated.

MERCURIC TELLURATES.

Berzelius described mercuric tellurate ($HgTeO_4$) as a white flocculent precipitate.

Divalent mercury forms two salts with telluric acid, mercuric orthotellurate (Hg_3TeO_6) and normal mercuric tellurate ($HgTeO_4$), both of which have been prepared in crystalline form. $HgTeO_4$ may be obtained as a white flocculent precipitate as described by Berzelius. Under favorable conditions it crystallizes with two molecules of water, giving $HgTeO_4.2H_2O$. The intermediate compound $3HgO.2TeO_3$ has not been isolated, although there are indications that it may exist. All precipitates of mercuric tellurate, whether crystalline or amorphous, show a strong tendency to change to mercuric orthotellurate in the presence of water. This property of mercuric tellurate renders it difficult to prepare $HgTeO_4$ in pure condition.

Mercuric Orthotellurate—Hg_3TeO_6.

When an excess of mercuric nitrate is added to a hot dilute solution of potassium tellurate, a heavy, yellow granular precipitate of mercuric orthotellurate is formed. In order to obtain this salt in crystalline form, a somewhat different method of procedure must be employed.

If a cold concentrated solution of mercuric nitrate is added to

a concentrated solution of potassium tellurate made acid with nitric acid, a white flocculent precipitate of $HgTeO_4$ is formed. At room temperature a portion of the precipitate usually assumes a yellow color immediately, probably due to the formation of a basic salt. If the acid solution containing this white or yellow flocculent precipitate is allowed to stand undisturbed for several days the precipitate is largely converted into transparent amber-colored crystals of Hg_3TeO_6. Frequently the walls of the containing vessel are covered with crystals that have separated from the acid solution. In many cases the amber-colored crystals form in contact with the white amorphous precipitate, but in all cases the crystals are entirely distinct from the precipitate.

Hg_3TeO_6 crystallizes in the isometric system, the predominating form being the dodecahedron. Combinations of the cube and dodecahedron are frequent, while many crystals show a broad octahedral face on which the crystal has grown. Single crystals have been obtained which are over an eighth of an inch in diameter. The crystals contain a little nitric acid and about 0.6 per cent. of water. This is considerably less than one-half of a molecule of water to one of Hg_3TeO_6.

The crystals are insoluble in water and unchanged by boiling with water. They are soluble in nitric acid but more readily soluble in hydrochloric acid.

When heated, the salt assumes a red color, but it regains its original color upon cooling. The crystals are not altered by heating to 140°.

Analysis of the salt, after having been dried over phosphorus pentoxide for several days, gave the following results:

4.6696 grams gave 0.0279 gram H_2O.

1.7853 grams gave 1.4940 grams HgS.

1.0894 grams with hydrochloric acid liberated chlorine equivalent to 0.1727 gram Te.

Found: Hg, 72.13 per cent.; Te, 15.85 per cent.; H_2O, 0.59 per cent.

The value obtained for tellurium is about 0.5 per cent. too high. This discrepancy is due to the presence of a little nitric acid in the crystals.

The corresponding sulphate of mercury, Hg_3SO_6, exists as turpeth mineral. This compound may be prepared as a heavy yellow powder or as yellow crystals by treating the normal sulphate

with water. In color the sulphate is very similar to the tellurate, but it does not crystallize in the isometric system.

Amorphous Hg_2TeO_4.

When concentrated solutions of mercuric nitrate and potassium tellurate or telluric acid are brought together at o°, a white flocculent precipitate of mercuric tellurate is formed. The precipitate is quickly decomposed by water at room temperature into telluric acid and basic mercuric tellurate. This decomposition goes on even when the precipitate is washed with water at o°; consequently, it is impossible to obtain a pure white product in suitable condition for analysis. The precipitate remains white indefinitely in a saturated solution of telluric acid at room temperature.

Analysis of the light yellow powder obtained by washing the white precipitate with water at o° showed that it approximates $HgTeO_4$ in composition.

Crystalline $HgTeO_4.2H_2O$.

If the white precipitate of mercuric tellurate formed by mixing concentrated solutions of mercuric nitrate and potassium tellurate containing free nitric acid, is allowed to remain undisturbed in the mother-liquor for several days at room temperature, nearly all of it is converted into crystalline Hg_3TeO_6. In some cases colorless crystals of $HgTeO_4.2H_2O$ were obtained mixed with the amber-colored crystals of mercuric orthotellurate.

It was found possible to prepare crystalline $HgTeO_4.2H_2O$ free from the basic salt by mixing concentrated solutions of telluric acid and mercuric nitrate at o° and allowing the resulting solution to stand at room temperature until the salt crystallized out.

Analysis of the colorless crystals gave the following results:

0.2413 gram gave 0.0202 gram H_2O.

0.2413 gram gave 0.0887 gram TeO_2.

	Calculated for $HgTeO_4.2H_2O$.	Found.
Tellurium	29.84	29.39
Water	8.41	8.37

$HgTeO_4.2H_2O$ appears as transparent crystals belonging to the orthorhombic system. It is slowly decomposed by cold water. Boiling water quickly decomposes it into telluric acid and basic mercuric tellurate.

Copper Orthotellurate, Cu_3TeO_6.

When a solution of copper nitrate is treated with a solution of potassium tellurate a green flocculent precipitate of copper tellurate is formed. Berzelius describes this compound as normal copper tellurate ($CuTeO_4$). If the precipitate is boiled for some hours with water it is converted into copper orthotellurate, which settles as a heavy green powder. It is insoluble in water but soluble in ammonia, potassium cyanide, and acetic, hydrochloric, and nitric acids.

Analysis of the green powder after having been dried over phosphorus pentoxide for a week gave the following result:

0.6675 gram heated with hydrochloric acid liberated chlorine equivalent to 0.2069 gram tellurium.

	Calculated for Cu_3TeO_6.	Found.
Tellurium	30.79	31.00

Numerous attempts were made to prepare copper tellurate in crystalline form, but none were successful. Copper hydroxide was treated with an excess of telluric acid; the resulting tellurate of copper was allowed to remain in the solution for several weeks. Likewise the precipitate obtained by bringing together solutions of potassium tellurate and copper nitrate was allowed to remain in mother-liquors of varying composition for weeks. In no case were the crystals of copper tellurate formed.

Zinc Orthotellurate, Zn_3TeO_6.

The white flocculent precipitate obtained by bringing together solutions of zinc nitrate and potassium tellurate may be changed into a heavy granular precipitate of Zn_3TeO_6 by long-continued treatment with hot water.

Analysis of the powder prepared in this manner and dried over phosphorus pentoxide for a week gave the following result: 0.6331 gram with hydrochloric acid liberated chlorine equivalent to 0.1940 gram tellurium.

	Calculated for Zn_3TeO_6.	Found.
Tellurium	30.40	30.64

Zn_3TeO_6 is insoluble in water but soluble in acetic, nitric, hydrochloric, and sulphuric acids.

Gutbier[1] prepared zinc tellurate in the form of a white insoluble precipitate by bringing together solutions of potassium tellu-

[1] *Z. anorg. Chem.*, **31**, 349.

rate and zinc chloride. He does not give the composition of the tellurate of zinc that he obtained in this manner.

Attempts were made to prepare zinc tellurate in crystalline form by allowing the amorphous salt to remain in contact with mother liquors of various compositions. The results were all negative.

Gold Tellurate.

No tellurate of gold has been prepared. From the experiments that have been made in attempt to prepare this salt it seems probable that water immediately decomposes the salt if it is formed in aqueous solutions.

When a solution of gold chloride is added to normal silver tellurate suspended in water, silver chloride and gold oxide are precipitated.

When solutions of normal potassium tellurate and gold chloride are brought together and the resulting solution allowed to evaporate over sulphuric acid, yellow crystals of potassium chloraurate are found. No tellurate of gold separates from the solution.

The fact that gold chloride takes up potassium from potassium tellurate to form potassium chloraurate is a good illustration of the weak affinity that telluric acid exerts towards bases.

SUMMARY.

(1) Telluric acid forms orthotellurates of the type M'_6TeO_6 with a number of metals. Ag_6TeO_6, Hg_3TeO_6, Zn_3TeO_6, and Cu_3TeO_6 have been prepared. The normal tellurates (*e. g.*, Ag_2TeO_4) of these metals are changed to the ortho compounds by treatment with water.

(2) The crystalline normal tellurates that have been prepared, *viz.*: $Ag_2TeO_4.2H_2O$, $Rb_2TeO_4.3H_2O$, $HgTeO_4.2H_2O$, $Cs_2TeO_4.3H_2O$, $Na_2TeO_4.2H_2O$, and $K_2TeO_4.2H_2O$,[1] may be considered acid salts of orthotelluric acid of the types $M'_2H_4TeO_6$ and $M'_2H_4TeO_6.H_2O$.

(3) Silver forms two crystalline tellurates—$Ag_2O.TeO_3.2H_2O$ and $3Ag_2O.2TeO_3.3H_2O$. The former salt is yellow and crystallizes in the orthorhombic system; the latter is red and crystallizes in the monoclinic system. Both of these salts may be considered

[1] Potassium forms a second tellurate—$K_2TeO_4.5H_2O$.

acid salts of orthotelluric acid. No selenate or sulphate of silver is known that is isomorphous with either of these salts.

(4) $HgHTeO_4.3H_2O$ crystallizes in the triclinic system. It is the only crystalline mercurous tellurate that has been prepared.

(5) Two crystalline salts of divalent mercury have been prepared, *viz.*: Hg_3TeO_6 and $HgTeO_4.2H_2O$. The former appears in the form of amber-colored crystals belonging to the isometric system; the latter is white and crystallizes in the orthorhombic system.

(6) The crystalline compound described by Oppenheim as a double salt of silver nitrate and tellurate is normal silver tellurate ($Ag_2TeO_4.2H_2O$).

(7) It has not been found possible to prepare the acid tellurates of silver described by Berzelius.

(8) Potassium tellurate may be prepared in crystalline form by slow evaporation of its solution, provided care is exercised to prevent supersaturation of the solution.

(9) Telluric acid does not completely replace the carbonic acid in an equivalent quantity of potassium carbonate. Crystalline normal potassium tellurate cannot be obtained from potassium carbonate and telluric acid as described by Berzelius.

(10) Although telluric acid is a weak acid, hot concentrated solutions of it attack mercury, silver, lead, tin, arsenic, antimony, bismuth, nickel, zinc, aluminum, and cadmium.

(11) There are no well authenticated cases of isomorphism between sulphates and tellurates or between selenates and tellurates.

[CONTRIBUTION FROM THE INSECTICIDE AND WATER LABORATORY, BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.]

A STUDY OF THE HYDROGEN PEROXIDE METHOD OF DETERMINING FORMALDEHYDE.

BY J. K. HAYWOOD AND B. H. SMITH.

Received July 2, 1905.

DURING the last year or two the authors have made use of the Blank and Finkenbeiner hydrogen peroxide method of determining formaldehyde, and have in the vast majority of cases obtained results which agreed with one another very satisfactorily and with the results obtained by other methods. However, a result would occasionally be obtained which was manifestly incorrect,

although the details of the method were followed closely. Besides this, other chemists who tested the same method were not always able to get closely agreeing results. It appeared, therefore, that there must be present certain disturbing factors which should be discovered before the method was adopted as a safe and correct one. With the above points in view the authors determined to make a comparative study of the various methods that have been proposed for determining formaldehyde by means of oxidation with peroxide, and, if possible, determine which was the best and on what factors was the error dependent.

The first method tested was the one usually followed by the authors which in detail corresponds closely to the original Blank and Finkenbeiner procedure.

Method.—Measure out 3 cc. of the formaldehyde (the specific gravity of which has been previously determined) into a flask containing 25 cc. of double normal sodium hydroxide, then add 50 cc. of pure 2.5 to 3 per cent. hydrogen peroxide with occasional shakings, in six to ten portions during three minutes, through a funnel placed in the neck of the flask to prevent spurting. Let stand three to five minutes (usually the latter), *shaking about every thirty seconds*, and finally titrate the excess of hydroxide with normal sulphuric acid, using litmus as indicator. Besides the above, seven- and fifteen-minute periods of allowing the hydrogen peroxide to act on the formaldehyde were also tried since it was possible that three minutes was not long enough to complete the reaction. On two samples, A and B, secured from the different manufacturers, the following results were obtained.

BY AUTHORS' PROCEDURE.

Time of action of total quantity of H_2O_2.	Per cent. of formaldehyde. A.	B.
3 minutes	36.90	36.92
7 minutes	36.99	37.02
15 minutes	36.90	37.11

It appears from the above that in one case at least a longer period than three minutes is necessary for complete oxidation of the formaldehyde; however, the difference between a three- and fifteen-minute period of action is small.

The next procedure tested was one recently suggested by Fresenius and Grünhut.[1] These authors discovered the following interesting facts in regard to the hydrogen peroxide method.

[1] *Z. anal. Chem.*, **44**, 16 (1905).

(1). That when the formaldehyde is added to the double normal sodium hydroxide solution there is danger of part of the formaldehyde acting on the hydroxide according to the equation $2HCHO + NaOH = HCOONa + CH_3OH$, before the peroxide is added, so that two equivalents of formaldehyde correspond to one equivalent of sodium hydroxide instead of the ratio being 1 : 1 as required by the Blank and Finkenbeiner method. (The equation followed in this method is either

$$HCHO + NaOH + H_2O_2 = HCOONa + 2H_2O$$

or

$$2HCHO + 2NaOH + H_2O_2 = 2HCOONa + 2H_2O + H_2.)$$

(2) That low and varying results are obtained if the flask is cooled during the time that the peroxide is acting on the formaldehyde.

Based on these observations they have suggested the following method of procedure which leaves the formaldehyde in contact with the sodium hydroxide a minimum length of time.

Method.—Weigh out about 3 grams of formaldehyde in a weighing-tube with a ground glass stopper. Place the tube in a flask containing 25 cc. of double normal sodium hydroxide, tip the tube over and immediately commence the addition of 50 cc. of 3 per cent. hydrogen peroxide. This addition is so regulated by dropping from a burette that three minutes is required for the entire addition, the flask being constantly shaken throughout this time. After standing two or three minutes with occasional shaking the excess of alkali is titrated just as before.

The following results were obtained by this method on A and B, one titration of the excess of alkalinity being made *immediately* after the addition of peroxide and the other four minutes after the addition.

PROCEDURE OF FRESENIUS AND GRÜNHUT.

Time of action of total quantity of H_2O_2.	Percentage of formaldehyde. A.	B.
0 minutes	37.04	36.92
4 minutes	37.04	37.02

It is evident from the above that one sample (A) was entirely oxidized as soon as the addition of peroxide was completed, while in the other case (B) a few minutes more were required for complete oxidation.

In the article just mentioned by Fresenius and Grünhut it was suggested that an addition of 5 cc. of hydrogen peroxide to the sodium hydroxide before the addition of formaldehyde might prove of advantage. This was tried and the results obtained were as follows: for A, 37.03 per cent. formaldehyde and for B, 36.79 per cent. formaldehyde. When the formaldehyde was allowed to stand in contact with the 5 cc. of hydrogen peroxide + 25 cc. of 2N soda before the extra 45 cc. of hydrogen peroxide were added, the percentage of formaldehyde was reduced in proportion to the time that this action was continued, thus showing that there is undoubtedly some action between the sodium hydroxide and formaldehyde according to the equation $2HCHO + NaOH = HCOONa + CH_3OH$.

Since there is this danger of the formaldehyde acting on the sodium hydroxide before the peroxide is added, it occurred to the authors that the simplest way to avoid any chance of such error is to add the total 50 cc. of peroxide to the soda before the addition of the formaldehyde and allow the mixture to stand long enough (with shaking about every thirty seconds) for the reaction to take place. This scheme was tried and the following results obtained:

Time of action of H_2O_2.	Per cent. of formaldehyde. A.	B.
5 minutes	33.89	30.39
10 minutes	37.22	34.44
15 minutes	37.28	37.17
20 minutes	37.28	37.17

It will be noted that constant results were obtained at the end of about fifteen minutes and that *these results are slightly higher than the results obtained by any of the other methods.* It was at first thought that this increase in the formaldehyde figure might be due to experimental errors, but the determinations were repeated a number of times with the same results. The explanation of this is, that in all the other methods there is some action directly between the formaldehyde and sodium hydroxide, either at the time when the formaldehyde is first added to the sodium hydroxide solution or more probably, later on in the reaction when the temperature has been raised and yet an excess of peroxide is not present (it being used up about as fast as it is added).

Since an error of 0.1 cc. in the reading of the double normal soda originally added corresponds to an error of about 0.19 per

cent. formaldehyde, an attempt was next made to carry out the method as just described but to use 50 cc. of normal instead of 25 cc. of double normal soda. The following results were obtained:

Time of action of H_2O_2.	Per cent. of formaldehyde. A.	B.
10 minutes	29.00	...
15 minutes	31.24	32.39
20 minutes	34.07	37.07
30 minutes	37.28	37.17

It is evident from this that normal soda can be used but the time necessary to complete the reaction is much increased. Several samples were tested by this method and it was found that it was not sure, *i. e.*, at one time the reaction would be completed in thirty minutes while at another time it would take forty-five minutes to complete it, another time forty minutes, etc. A probable explanation of this marked slowing of the reaction was sought in the statement made by Fresenius and Grünhut that low, varying results are obtained if the flask is cooler during the time that the peroxide is acting on the formaldehyde. In this case, to be sure, the flask was not cooled, but it was more dilute, which practically amounted to cooling in that the heat of reaction had to raise the temperautre of a much larger body of liquid. Observations were made of the temperatures attained in all of the methods described above, and it was found that the time necessary to complete the reaction was a direct function of the temperature reached, so that in the procedures where a maximum temperature was attained the reaction took place in the shortest length of time. This being so, an attempt was made to hurry the reaction between the peroxide and formaldehyde in the presence of normal soda by keeping on the steam-bath. The following results were obtained:

Time of action of H_2O_2.	Per cent. of formaldehyde. A.	B.
5 minutes	37.22	37.21
10 minutes	37.22	37.21

It is evident from this that the greatest factor in decreasing the time necessary for the completion of the reaction is a sufficiently high temperature. If the temperature is raised to 100° C., the reaction will take place very quickly.

Based on the above experiments the following procedure for

carrying out the Blank and Finkenbeiner method has been adopted by the authors. It has been tested on a number of samples and has been found to always lead to safe, accurate results with the expenditure of a minimum amount of time and attention.

Method.—Measure out 50 cc. of normal sodium hydroxide in a small Erlenmeyer flask (say of 500 cc. capacity) and add 50 cc. of pure 3 per cent. hydrogen peroxide. Now add from a pipette 3 cc. of the formaldehyde solution under examination (the specific gravity of which has been previously determined), allowing the point of the pipette to almost reach the liquid in the flask. Place a funnel in the neck of the flask and put on the steam-bath for five minutes, shaking occasionally during this time. Remove from the steam-bath, wash the funnel with distilled water, cool the flask down to about room temperature and titrate the excess of sodium hydroxide with normal acid, using litmus as indicator. This cooling of the flask before titration with acid was found necessary so as to get a sharp end-reaction with the litmus. From the volume of formaldehyde used and the specific gravity, the percentage by weight of formaldehyde can be determined.

INNER CRUCIBLE METHOD FOR DETERMINING SULPHUR AND HALOGENS IN ORGANIC SUBSTANCES.

By S. S. SADTLER.

Received July 21, 1905.

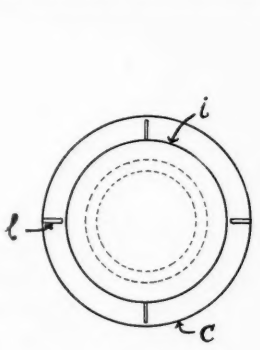
TO ALL workers in organic chemistry who have to make determinations of sulphur and halogens in research or commercial work, the use of the Carius furnace is almost always found troublesome. It has always been so to the writer, and after many plans to avoid its use, he devised the way to be here described.

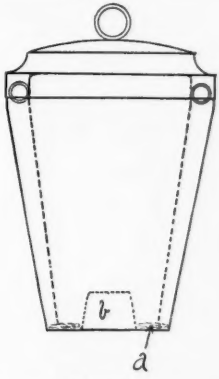
The general idea does not seem to be a new one, as Dr. Edgar F. Smith said in discussion upon an unpublished paper read by the writer before the Philadelphia Section of this Society, that he had used an inverted inner crucible with caustic lime as a reagent to determine chlorine in organic substances when a student. More recently Shimer[1] described an inner crucible method for determining carbon in steel, etc. The writer tried inverting small platinum and porcelain crucibles in large platinum crucibles, but with sulphur compounds containing volatile constituents the oil

[1] *Chem. Eng.*, November, 1904.

not only began to distil before the absorbing layer of the reagent became sufficiently heated to take up the sulphur, but also came off too fast.

Successful results even with fairly volatile oils containing sulphur were finally obtained by modifying the inner crucible so as to meet the requirements. It was made at first of sections of glass combustion tubing, the idea being to keep the charge to be analyzed as far as possible from the point of application of the heat, and to have a relatively poor conductor of heat, which was readily obtained with glass. The charge was put in the rounded end, which had been drawn out to seal it, and packed with Eschka mixture. This made a fairly satisfactory apparatus for, while the absorbing mixture became red hot, the oil was only gradually vaporized. It was found, however, that the glass was acted upon by the alkaline mixture and sulphur seemed to be taken up at times in an adhering mass in one determination and given off in another. An ordinary 20-gram platinum crucible was used for the outer crucible. The inner crucible of glass, however, was not considered practicable and a cylinder of platiunm closed at the upper end was tried, and it was found that the Eschka mixture used expanded with heat and lifted the cylinder. The following apparatus was, therefore, tried after other intermediate attempts, and found to be satisfactory.





a Layer of pure asbestos.
b Indentation in outer crucible.
c Outer crucible.
l Ring-shaped lugs.
i Inner crucible.

Dimensions.
Large crucible—2 inches high (for oils, etc., low in sulphur).
Small crucible—1½ inches high (for oils, etc., containing more than 0.5 per cent. sulphur).

PLATINUM APPARATUS.

The outer crucible is made with straight sides like an inverted

truncated cone with a tightly fitting lid. In the bottom is a cylindrically shaped indentation so as to extend the highly heated zone into the inner crucible.

The inner crucible was made with sides very nearly parallel to the outer crucible when inverted within it. Small rings of platinum were soldered to the wide, closed end, so as to keep it centered with respect to the outer one.

The open end is made as thin as possible so as to minimize the tendency to conduct heat. The edge fits about midway between the walls of the central indentation and the outer crucible.

PROCEDURE.

The method of procedure varies somewhat with the material for analysis. With solids careful insulation of the two crucibles is not necessary. With liquids, especially those containing sulphur, careful insulation is requisite, and with very volatile ones, such as carbon disulphide, it is necessary to fill them into small capillary bulbs such as are used for sealed tube combustions.

An important difficulty in the way of getting accurate results with this method was the puffing of the Eschka mixture, and the author found that the chemically pure light magnesia he was using contained 12 per cent. of water, and when this was driven off, and carefully dried sodium carbonate was used, that lifting the crucible and puffing ceased. The mixture was made up of equal weights of dried magnesia and sodium carbonate instead of 2 to 1.

The substance is first weighed into the inner crucible, which is placed open end up on the balance pan. It is found desirable to take the minimum weights which will give final precipitates suitable for weighing. Thus about 1 gram of sulphur compound containing 1 per cent. sulphur is taken.

An amount of a halogen compound containing about 1/20 gram of actual halogen, depending somewhat upon the one in question, and about the same amount of phosphorus-containing substance.

Enough mixture is then put in to absorb the substance, when it is a liquid, and then filled nearly to the top with moderate tamping. Plain ignited magnesia is then put in level with the top, so as to keep the soda away from the platinum, as the platinum on the bottom of the crucible is attacked by the hydrate of soda which is formed at the high temperatures or some compound with reducing gases.

Freshly ignited, white asbestos is then put around the raised portion of the bottom of the outer crucible to keep the two crucibles from being in actual contact. It is then lowered over the inner crucible and then both crucibles inverted. A layer of magnesia mixture about one-fourth inch deep is then put in between the crucibles. The outer crucible is then put through a hole in a piece of thin but firm asbestos board so that very little, if any, of the sides can be exposed to the direct action of the flame.

A very small pointed flame of a Bunsen burner is now used so that the flame is chiefly in the indentation on the bottom. If gases do not come off from the crucible in three to five minutes with this flame, the heat is increased, and when no more odor is noticeable the crucible is placed in a piece of asbestos having a larger hole, so that half of the crucible may become red hot and is kept so for ten minutes. The flame is then withdrawn, and when cool the inner crucible is carefully raised and tapped, so that its contents are dropped into the outer one, when the carbon is burned out with a shield of asbestos to protect the contents from the sulphur gases of the flame in the case of sulphur determinations.

For sulphur determinations the contents of the crucibles are washed into a beaker. Bromine is added to oxidize sulphites, etc., the solution is filtered, acidified and precipitated with barium chloride as in the case of determinations of sulphur in coal.

With halogen compounds the contents are washed into a beaker, and dissolved with pure nitric acid, the asbestos filtered off and the halogen precipitated by means of silver nitrate. The chief precaution the author has found necessary is to bring all the contents of the charge to red heat to break up any oxygen compounds of chlorine.

In the case of phosphorus the writer is undecided as to whether there is any real necessity in using this method, but as metaphosphates give off phosphine gas when heated, it seems probable that this method would be found useful. The entire contents of both crucibles must be dissolved in nitric acid and filtered, and then molybdate solution added in the usual way. On dissolving the yellow precipitate, a white crystalline precipitate ($Mg_3(PO_4)_2$) may be found, which must be redissolved in a little nitric acid and added to the ammoniacal solution to which magnesia mixture is to be added.

This method, so far as the writer has been able to investigate it, applies to all organic combinations of sulphur, the halogens and phosphorus, but the amount taken must be limited to take only a moderate final weight of barium sulphate or silver halide, such as 0.1000 to 0.2500 gram.

RESULTS OF ANALYSES.

Sample.	Carius.	Inner cone crucible.
1. Texas crude oil	1.70	1.709
2. Texas gas oil	0.40	0.39–0.41
3. Ohio crude oil	0.99	1.03–1.05
4. Ohio gas oil	0.36	0.32–0.32
5. Kansas crude oil	0.62	0.57–0.59

The writer has made a number of analyses of organic combinations of sulphur, chlorine and bromine, but owing to the incomplete character of the results at this time, he prefers to reserve the work of investigating the use of the crucible for halogen compounds for a later publication.

The author wishes to express his indebtedness to J. Bishop & Company for kindness in making four different sets of crucibles for this work.

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A SIMPLE COLORIMETER FOR GENERAL USE, WITH REMARKS ON COLORIMETRIC METHODS AND APPARATUS.[1]

BY OSWALD SCHREINER.

Received June 22, 1905.

THE USE of colorimetric methods for the estimation of small amounts of materials has been on the increase in the past few years, not only in technical analysis but also in other lines of investigation. The applications of colorimetry to the determination of ammonia, nitric and nitrous acids, has been of long standing and these tests are familiar to every chemist. They have been used by the sanitary chemist for some time, and to these has lately been added the colorimetric determination of phosphates for detecting polluted waters. The mineralogical chemist has likewise recognized in the colorimetric tests for certain metallic elements the best, and in some cases the only, method for deter-

[1] Published by permission of the Secretary of Agriculture.

mining small quantities of these substances. The industrial chemist has used colorimetric methods as a ready and accurate means of valuation in the most varied industries, and the food analyst is also using them for detecting and estimating the extent of adulteration in foods and beverages, and injurious products in whiskies. The physiologist and the pharmacologist have found the application of these methods useful in the problems with which he has to deal, and the physical chemist and agricultural chemist have also applied them in the course of their studies on the solubility of glass, minerals and other difficultly soluble substances and in the study of the phenomena of adsorption.

How general the use of colorimetric methods has become in recent years, not only in their application to inorganic compounds, but also to the principal classes of organic compounds, may be illustrated by the following brief and therefore very incomplete presentation. In inorganic chemistry colorimetric methods have been worked out or suggested; for metals (such as alkalies,[1] chromium,[2] copper,[3] iron,[4] manganese,[5] magnesium,[6] potassium,[7] titanium,[8] tungsten,[9] etc.); for non-metals (such as carbon,[10] sulphur as sulphide[11] and sulphuric acid,[12] oxygen[13] as element and as hydrogen peroxide,[14] arsenic as arsenious acid,[15] phosphorus as phosphoric acid,[16] nitrogen as nitrous and nitric acids and as ammonia,[17] boron as boric acid,[18] etc.).

The use of photometric and nephelometric methods still further increases the list of metals and non-metals of which small amounts

[1] Mylius and Förster: *Z. anal. Chem.*, **31**, 250 (1892).

[2] See Hillebrand: "Some Principles and Methods of Rock Analysis," Bull. 176, U. S. Geol. Survey, p. 80.

[3] See Sutton's "Volumetric Analysis," and other texts.

[4] See Pulsifer: This Journal, **26**, 974 (1904).

[5] Marshall: *Chem. News*, **83**, 76 (1901); Clennell: *Eng. Min. J.*, **78**, 827 (1904). See also Blair's "The Chemical Analysis of Iron," and other texts.

[6] Schreiner and Ferris: This Journal, **26**, 961 (1904).

[7] Hill: This Journal, **25**, 991; Cameron and Failyer: *Ibid.*, **25**, 1063 (1903).

[8] See Hillebrand: *Loc. cit.*, pp. 67 and 73.

[9] Frabot: *Ann. Chim. Anal.*, **9**, 371 (1904).

[10] See Blair: "The Chemical Analysis of Iron," and other standard works.

[11] Winkler: *Z. anal. Chem.*, **40**, 772 (1901); Lindlay: *School of Mines Quarterly*, **23**, 24 (1901).

[12] Winkler: *Z. anal. Chem.*, **40**, 465 (1901).

[13] Ramsay and Honefray: *J. Soc. Chem. Ind.*, **20**, 1071 (1901).

[14] Richardson: *J. Chem. Soc.*, **63**, 1109 (1893); Planes: *J. Pharm. Chim.* [6], **20**, 538 (1904).

[15] Peck: *Trans. Brit. Pharm. Conf.*, p. 452 (1901); Mai: *Z. anal. Chem.*, **41**, 362 (1902).

[16] See Schreiner and Brown: This Journal, **26**, 1463 (1904); Hewitt: *Ibid.*, **27**, 121 (1905).

[17] See Wiley's "Agricultural Analysis," and other standard texts.

[18] Hebebrand: *Z. Nahr. Genussm.*, **5**, 55 (1902); Cassal and Gerranz: *Chem. News*, **87**, 27 (1903).

can be quite accurately determined (such are, calcium,[1] sulphur as sulphates,[2] chlorine,[3] silver,[3] mercury,[4] etc.). In the field of organic chemistry, colorimetric methods have received wide application. The large number of color reactions shown by nearly all classes of organic compounds make the application of the principles of colorimetry especially fruitful in this field. They have been used in the determination of alcohols (ethyl alcohol,[5] etc.); of aldehydes (acetic aldehyde,[6] vanillin,[7] etc.); of acids (salicylic,[8] tannic,[9] etc.); of esters (ethyl nitrite[10]); of phenols (phenol,[11] cresol[12]); of carbohydrates (sugar,[13] glucose,[14] starch,[15] etc.); of alkaloids (morphine,[16] caffeine[17]); of haemoglobin,[18] chloroform,[19] etc. The photometric and nephelometric methods have also found application for determining small amounts of organic compounds (such as albumen,[20] citric acid,[21] etc.). It is needless to add that the principles of colorimetry are employed in the investigation of the artificial as well as natural dyes, as for instance in the valuation of indigo,[22] saffron,[23] the various dye woods, the aniline dyes as well as the dye content in technical dye liquors.

In devising colorimetric methods there have been two main objects throughout, namely, speed and the ability to estimate small amounts, both of which are common to many of the methods,

[1] Hinds: This Journal, **18,** 661 (1896); *Ibid.*, **22,** 269 (1900).
[2] Hinds: *Loc. cit.*; Jackson: This Journal, **23,** 779 (1901).
[3] Richards and Wells: *Am. Chem. J.*, **31,** 235 (1904).
[4] Eschbaum: *Pharm. Ztg.*, **47,** 260 (1902).
[5] Argenson: *Bull. Soc. Chim.*, **27,** 1000 (1902).
[6] Paul: *Z. anal. Chem.*, **35,** 647 (1896); Francois: *J. Pharm. Chim.* [6], **5,** 521 (1897); Argenson: *Loc. cit.*
[7] Dietrich: *Z. anal. Chem.*, **37,** 453 (1898).
[8] Langkoff: *Pharm. Centralhalle,* **41,** 335 (1900); Conrady: *Apoth. Ztg.*, **15,** 412 (1900); Harvey: *Analyst,* **28,** 2 (1903).
[9] Hinsdale: *Chem. News,* **64,** 51 (1891).
[10] Cowley and Catford: *Pharm. J.*, **63,** 471 (1899).
[11] Carré: *C. R.*, **113,** 139 (1891).
[12] Schneider: *Rep. Soc. Germ. Nat. and Phys.*, Sept., 1895; *Amer. Drugg.*, **28,** 252 (1895).
[13] Neitzel: *Z. Spiritusindustrie,* **20,** 163 (1896).
[14] Ruini; *Gazz.*, **31,** 445 (1901); Lyons: *Pharm. Rev.*, **20,** 155 (1902).
[15] Dennstedt and Voigtländer: *Forschungsb. ü. Lebensmittel,* **2,** 173 (1896); Ambuhl: *Chem. Ztg.*, **19,** 1508 (1895).
[16] Palmer: *Merck's Report,* **11,** 191 (1902).
[17] Archetti: *Apoth. Ztg.*, **15,** 110 (1900).
[18] Hoppe-Seyler: *Z. physiol. Chem.*, **16,** 505 (1892); Zangemeister: *Z. Biol.*, **33,** 72 (1896); Haldave: *J. Physiol.*, **26,** 497 (1901).
[19] Seyda: *Z. öffentl. Chem.*, **3,** 333 (1897).
[20] Riegler: *Pharm. Centralhalle,* **38,** 349 (1897); Guerin: *Apoth. Ztg.*, **14,** 726 (1899).
[21] Deniges: *C. R. Soc. Biol.*, **54,** 197 (1902).
[22] Koppeschaar: *Z. anal. Chem.*, **38,** 1 (1899).
[23] Vinassa: *Arch. Pharm.*, **231,** 353 (1892).

but not necessarily so. A colorimetric method may have speed and yet not be capable of estimating very small amounts. Speed is, through necessity perhaps, of the greatest importance to the works chemist and to the busy analyst. The ability to estimate very small amounts of material, however, is of the greatest importance to the modern investigator in the field of pure and applied sciences, and to him speed is of only secondary importance if indeed he values it at all. Some of the more recently devised colorimetric methods are for this very reason fully as laborious and perhaps even more tedious than the gravimetric methods, and their one virtue lies in the fact that they can be used in determining amounts so small that gravimetric methods fail, and hence they present a means of attacking problems which hitherto had been impossible of investigation.

The choice whether a gravimetric[1] or a colorimetric method should be used in a given case lies therefore almost wholly within that class of colorimetric methods which have been devised for speed, and the question in this case is usually only one of comparative accuracy as balanced by the gain in time. This gain in time may, however, be of the utmost importance, not only in a works laboratory, but also in a scientific investigation where it is necessary to know the amount of a substance present at any given time in the course of an experiment. In the second type of colorimetric methods, no choice between a gravimetric and a colorimetric method exists, when small amounts are involved. When larger quantities are available, the choice should always be in favor of the gravimetric method, providing, of course, that a reliable gravimetric method exists for the particular substance under investigation. When speed is also a consideration in the method this will somewhat complicate the choice between a gravimetric and a colorimetric method, and the needs of the immediate problem under consideration must guide the analyst.

As to the accuracy of the colorimetric methods no general statement can be made. Some colorimetric estimations have been brought to such a degree of perfection that they far surpass gravimetric determinations in accuracy. On the other hand, many of the colorimetric estimations are only gross approximations, but even these serve a purpose, for in such cases we usually have no other means of estimating the substance. It is, however, between

[1] These remarks apply to volumetric methods as well.

these two extremes that the majority of the methods lie. Folkard,[1] Krüss[2] and many others have pointed out the extreme degree of accuracy which is attainable with such methods when carried out with care, and there is little doubt that their accuracy is more frequently underestimated than overestimated. This is due to a number of causes, chief among which are the inability on the part of many persons to judge colors accurately, contamination while making the tests, the use of impure reagents, and the employment of faulty apparatus. Practice will do a great deal to enable one to make good comparisons, but it can never make up for a dulled or imperfect susceptibility to color. Great attention should be given to this point and the operator should test himself thoroughly by matching a standard against itself in several degrees of intensity. If no concordant results can be reached by practice in this way it is useless to go further with this color, but it may, nevertheless, be possible for him to read accurately some other color. Several cases of this kind have come under the author's observation while training assistants in these methods, and a man who cannot use one method with accuracy is frequently able to use another method with great precision. The use of impure reagents and contamination while carrying out the test are, of course, inexcusable, yet they have led to disparaging remarks concerning the application of colorimetric methods. One criticism frequently made is that merely diluting the standard solution to one-half its strength caused the unknown solution to be found only one-third as strong as had been found when measured against the full standard. It is obvious that had the half standard been measured against the full standard it would have been found that this was of much greater intensity than it should have been. This result could only have been obtained by gross contamination, which with the substance in question was very probable, even with distilled water as usually prepared in laboratories. It is, of course, possible that in this case the ability to judge the particular color was at fault.

The apparatus used in colorimetry is worth consideration from the point of view of accuracy, but at the same time the importance of speed must not be overlooked. A large number of colorimeters have been devised, but it would be impracticable to

[1] *Chem. News*, **75**, 73 (1897).
[2] "Kolorimetrie u. Quantitative Spektralanalyse" (1891).

discuss the various forms here, and it must therefore suffice to outline briefly the three types of apparatus and procedures in most common use. In one of these the comparison vessels consist of a pair of parallel walled cells into which the standard and unknown solutions are put and then diluted until both are of equal intensity. In this type then, the length of column viewed by the observer remains constant and the equality of color is regulated wholly by dilution. The comparison is made in a suitably constructed camera. This general procedure is accurate but quite tedious.

A second type of procedure, and the one usually followed, has many objections and is likewise quite tedious if very accurate results are desired, as it involves a great many separate tests and comparisons. It consists in developing the color in equal volumes of the unknown solution and solutions of known strength, selecting the ones which come nearest to it in intensity and then repeating, this time within narrower limits, until a strength of known solution is found which exactly corresponds with that of the unknown. The apparatus used for making the comparisons consists of glass cylinders, preferably with polished glass bottoms, on which have been etched capacity marks, such as 25, 50 or 100 cc. Such tubes as are found on the American market are very faulty in their construction and only too often are made of very poor and tinted glass. The bottoms are exceedingly irregular and the capacity marks vary greatly in their height from the bottom of the tubes, so that it is highly essential that only well "matched" pairs of cylinders be used in making tests. Moreover, the tubes are usually quite tapering so that the lower 50 cc. will occupy an entirely different height from the upper 50 cc. This difference in height amounts to as much as 10 per cent. in tubes obtained from the most reliable American firms. It is, of course, the length of the column of liquid and not the volume which determines the intensity of the image viewed, and in such cases the operator is therefore always dependent upon the coincidence of both volume and height in the tubes used; in other words he must have a pair of well "matched" tubes.

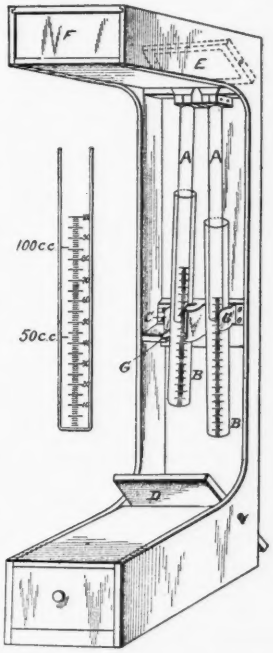
In the third procedure the height of the standard column is changed until the intensity is the same as that in the unknown solution. This is by far the most speedy and when the proper conditions are observed it is also the most accurate of the pro-

cedures mentioned. This change in the heights of the solution has been accomplished in a variety of ways; by dropping from a burette into one of the above tubes, by providing such a tube with a stop-cock at the bottom, by connecting by means of a side tube at the bottom with a reservoir which allows moving the liquid up or down at will, and by changing the height by means of an immersion prism or tube. Curiously enough, the graduation into cubic centimeters has been carried over to the cylinders used in many of these instruments when it is perfectly obvious that it is the height of the standard liquid which determines the strength of the unknown solution. In these forms of apparatus the above-mentioned irregularity in the bore of the tubes becomes a vital defect when a cubic centimeter scale is used. The following conditions must therefore be complied with in graduating such a pair of tubes if they are to be used for accurate work: One of the cylinders must be uniform throughout its bore, a condition not easily met. On this are etched 50 and 100 cc. marks. The height of the 100 cc. mark is laid off on the comparison cylinder, which is to contain the known standard, and is provided with the outlet at the bottom. The distance from this mark to the bottom of the tube is divided into 100 equal divisions. In other words, the scale on the standard solution tube is really the scale which reads cubic centimeters in the unknown solution tube. If, therefore, the latter should be broken, the graduated tube has lost its value, for it would be difficult to find another tube which would correspond to this scale. The use of the cubic centimeter scale in graduating such colorimetric apparatus is entirely wrong in principle and should be abandoned. A rational graduation into scale divisions independent of capacity and therefore of the size or uniformity of the bore of the tube, is used in the instrument described below.

For some years this Bureau has been carrying on a series of studies in which the estimation of small amounts of mineral plant food constituents was of the utmost importance. Known colorimetric methods were adopted or new ones devised for this purpose, and as speed and ready manipulation, so far as the handling of the apparatus was concerned, were also of great importance in order to make possible the large number of determinations necessary in order to accomplish the work, especial attention was paid to constructing a simple, accurate and speedy apparatus for making

colorimetric readings. The writer is under obligations to Prof. F. H. King for many practical suggestions and help in constructing the colorimeter. This instrument is the one used throughout the work described in Bulletin No. 26 of this Bureau, and has been found so useful in other colorimetric work during the last two years that it was thought of sufficient interest to bring it to the attention of chemists generally.

The working parts of the instrument, that is, those parts which come in contact with the solutions, are entirely of glass, mounted in a suitable camera of wood, as shown in the accompanying figure.



In its simplest form the colorimeter consists essentially of graduated glass tubes containing the standard and unknown colorimetric solution, the column of liquid in both tubes being changed by means of two smaller immersion tubes, also of glass. The immersion tubes *A* are 26 cm. in length and about 2 cm. in diameter and resemble the narrow Nessler tubes, the bottoms being well ground and polished. The upper ends of the tubes are mounted in blocks of wood which fit into grooves on the body of the colorimeter. This permits the ready removal of the tubes from the colorimeter for cleaning when the liquids are changed. The graduated tubes *B* have well-ground bottoms and are likewise 26 cm. in length, but have a diameter of about 3 cm. The scale divisions are 2 mm. apart. On the reverse side of the tube there are 50 cc. and 100 cc. marks for making the solutions up to definite volume. These tubes are supported by a block of wood about midway of the camera and are held in place by brass springs or clamps *C*, the tension of which can be regulated to suit the diameter of the tube, so as to allow it to be moved freely up or down by hand and yet be firmly held in position when the setting is

made. It will be noticed from the figure that the glass tubes diverge slightly. This has been found of advantage, as it allows the operator to look down the center of both immersion tubes, as well as to bring the upper parts of the tubes, and consequently the images closer together. The openings to the immersion tubes can be covered by means of a microscope slide to prevent dust from falling into the tubes. The tubes are illuminated from the reflector D below, which carries a sheet of white cardboard or opal glass, and after passing through the tubes the light is reflected by a mirror E in the upper part of the instrument to the eye of the observer at F. The mirror E should, as far as practicable, be of colorless glass, as the greenish color of ordinary glass has a tendency to change the quality of the light and interfere in the estimation of weak solutions. This is especially true of the yellowish green color of the phosphomolybdate solutions obtained in the estimation of phosphates. The dimensions of the camera are about 70x32x16 cm.

To make the comparison the standard colorimetric solution is poured into one of the graduated tubes and put into place in the camera together with the immersion tube. The unknown colorimetric solution, made up to definite volume, is put into the other graduated tube and similarly placed in the instrument. The tube containing the solution of unknown strength is set at a convenient height, say fifty scale divisions, and the other tube containing the standard moved up or down, the operator watching the effect on the images in the mirror through the opening at the front of the camera. By moving the standard tube so that the image is alternately weaker or stronger than that of the unknown solution the setting can be accurately and quickly made. When both images show the same intensity of color, the setting is read by noting the division mark on the graduated tube opposite the ground bottom of the immersion tube. This reading will give the height of column of the standard which exactly corresponds with the intensity of color of the column of the unknown solution. It follows that the strengths of these two colorimetric solutions are inversely as the heights of the columns, that is, as the readings on the two tubes. If R is the reading of the standard solution of strength S, and r the reading of the colorimetric solution of unknown strength s, then

$$s = \frac{R}{r} S.$$

The same formula, of course, applies when the standard is fixed and the unknown solution moved up or down until the images are of equal intensity.

Standard glass slides may be inserted at G below one of the immersion tubes in place of the tube containing the standard solution, the immersion tubes being retained so as to give similar images when viewed from above. The Lovibond slides have been used for this purpose, the constant C for the slide being obtained by the formula

$$C = RS,$$

where R is the reading of the standard of strength S when the two images are of equal intensity. The simple colors can be used in some cases, such as the yellow for the nitrate method, but usually a combination of colors will be required to match the color of the solutions and this complicates the use of the slides considerably. A series of slides, of different intensities, but bearing a simple relation to each other, are necessary in order to measure both strong and weak solutions. The strength s of the unknown colorimetric solution, when measured against such a slide, is found by the formula

$$s = \frac{C}{r},$$

where C is the above-mentioned constant for the slide used and r the reading of the unknown solution. These slides are especially serviceable as a control for checking the standard solutions from day to day where the use of the latter is preferred.

In carrying out accurate tests it is highly essential that the standard solutions be carefully prepared and protected from any contamination, such as with the ammonia and nitrite standards, the phosphate standard where contamination by silica is very apt to take place, and many others. In many cases deterioration of the standard itself must be carefully guarded against, such as the aldehyde standard, where aldehyde ammonia is used. The solutions must be perfectly clear with no suspended particles whatever. They should both be at the same temperature, as the absorption spectrum of colored compounds and consequently the color of the solution changes with the temperature. The solvent itself has an absorption effect on the light and hence it is always advisable not to have the concentration of the unknown solution vary widely from that of the standard. It is better in this case to

dilute the standard to a similar order of intensity with freshly distilled water. By this procedure the colors are likewise better compared as the absorption spectrum and consequently the transmitted color of many of the dyes is quite different in concentrated solution from what it is in more dilute solutions.

The glass parts of the colorimeter have been made for this Bureau according to the following specifications: The measuring colorimeter tubes are to be 26 cm. long, with *inside* diameter as nearly as practicable 27 mm.; in no case less than 25 mm., and not greater than 29 mm. The glass is to be colorless and the bottoms well ground and polished, with the internal surfaces of the bottoms plane, in no case appreciably convex or concave ; the bottoms to be ground down sufficiently so as to make the ground surfaces a little larger than the internal diameters of the tubes, each of the tubes to be provided with an etched scale of 100 two-millimeter divisions. The scale is to begin at the level of the inner surface at the bottom, the length of the marks being 6 mm., and every fifth mark 12 mm., numbering every tenth mark, on the right side, 10, 20, 30, etc., beginning at the bottom. On the reverse side of each measuring tube there are to be etched two capacity marks, one for 50 cc., and the other for 100 cc. The smaller tubes are likewise 26 cm. long, with *outside* diameter not greater than 20 mm., and not less than 18 mm., with the thickness of the glass the same in all the tubes. The bottoms of these tubes are to be carefully ground and polished and the inside of the bottom never sensibly convex or concave. They must be of colorless glass with the bottoms so ground that the diameter of the ground portion exceeds the internal diameter of the tube. These tubes are to be provided with neither scale nor capacity marks.

The tubes furnished by the makers of glass apparatus leave much to be desired. The bottoms of the tubes can, according to the statements of these makers, be ground and polished only on the outside, and this leaves the inner surface uneven, and slightly concave. For very accurate work, tubes with plates of plane glass cemented on the bottom are strongly recommended as the images obtained in this case are perfectly bright and free from all the objectionable features introduced by light passing through the uneven and somewhat concave bottoms of the ordinary tubes, which act as plano-concave lenses. The objectionable feature is the cement, which, with continued use of the alkaline or acid

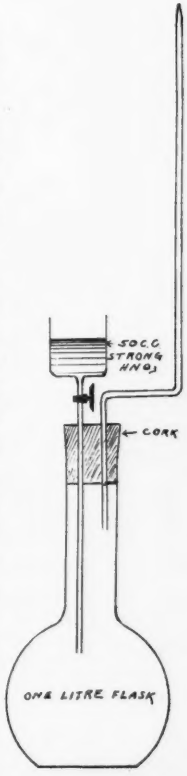
media of many of the colorimetric solutions, is rapidly disintegrated, and the tube will have to be replaced by another until repaired. When a colorimeter is in almost continued use, this loosening of the cement is very troublesome and the more faulty tubes with permanent glass bottoms above described have been found on the whole to be the most satisfactory for routine work in the laboratory and especially so for the field work, reserving the more perfect tubes with cemented bottoms for use in occasional research problems in the laboratory.

BUREAU OF SOILS,
U. S. DEPARTMENT OF AGRICULTURE,
WASHINGTON, D. C.

NOTES.

Note on the Gravimetric Determination of Sulphur in Iron and Steel.—In the gravimetric method for the determination of sulphur in iron and steel, the well-known danger of escape of unoxidized sulphur during the period of the violent action of the solvent nitric acid on the drillings may be obviated by the following method of solution.

Five grams of drillings are placed in a liter flask fitted with a doubly perforated cork. In one perforation is fitted a funnel-tube with a stop-cock. In the other is fitted a piece of quarter-inch glass tubing which extends about eighteen inches above the flask and is drawn to a point at the end out of the flask. The stop-cock being closed, introduce about 50 cc. strong nitric acid into the funnel tube. Open the stop-cock so that the acid runs into the flask at a rate not greater than two drops per second. When all the acid has passed into the flask, shut the stop-cock and heat the flask gently until solution is complete. The solution is then transferred to a dish. It is advisable to char the cork on its smaller end to prevent the oxides of nitrogen from acting on it.



After solution is complete the contents of the flask are transferred to a porcelain dish, the flask rinsed with concentrated hydrochloric acid, and the solution brought just to dryness, *not baked*, over a low flame. The residue is dissolved in 40 cc. of concentrated hydrochloric acid, evaporated nearly to dryness, diluted and filtered. The filtrate is heated to incipient boiling and 10 cc. of a 10 per cent. solution of barium chloride are added. The solution is again evaporated till crystals of ferric chloride appear, diluted with 175 cc. of cold water and allowed to stand six hours at room temperature or two hours in running water. We have found this precaution very necessary because of the solvent action of an acid solution of ferric chloride upon the barium sulphate.

In our experience, when the drillings are fine and solution is effected quickly, the evolution method gives with *foundry* irons results which agree very closely with those obtained by the gravimetric method.

The following results illustrate the concordance of the two methods:

	Evolution method. Titration with iodine of theoretical strength.	Gravimetric method as described.
1	0.078	0.079
2	0.083	0.083
3	0.108	0.109
4	0.073	0.072

The same agreement cannot, of course, be obtained with mottled or white irons.

CHARLES R. MCCABE.

MONESSEN, PA.

Note on the Atomic Weights of Carbon and Beryllium.—At the Philadelphia meeting of the American Chemical Society, Prof. F. W. Clarke, chairman of the International Committee of Atomic Weights, called my attention to the fact that my determinations of the equivalent of beryllium[1] being made on two compounds containing the same elements could be calculated entirely independent of the accepted factor for carbon; that the atomic weight of carbon could likewise be obtained independent of that of beryllium from the general average of the same determinations; that then both would depend solely upon the accuracy of the work itself and upon the accepted ratio between hydrogen and oxygen, and that a good value thus obtained for carbon would be excellent confirmation of the accuracy of my results on beryllium.

[1] This Journal, **26**, 721.

This method of calculation by simultaneous equations was first applied by Strecker[1] in a discussion of Liebig and Redtenbacker's data relative to the atomic weight of carbon, and was afterwards applied by Clarke[2] in a discussion of Partridge's work on cadmium and later[3] in regard to its more general application.

Applying this principle to the general average of each set of my determinations a new figure is obtained for both carbon and beryllium.

As an average of seven analyses of beryllium acetylacetonate[4]

$$Be(C_5H_7O_2)_2 : BeO :: 2.18109 : 0.26422$$

whence, subtracting the BeO from the first factor and letting

$$BeO = x,\ C = y,\ H = 1.008 \text{ and } O = 16$$

$$10y + 62.112 : x :: 1.91687 : 0.26422$$

or

$$(a)\quad 1.91687x - 2.6422y = 16.4112326.$$

As an average of nine analyses of basic beryllium acetate[5]

$$Be_4O(C_2H_3O_2)_6 : BeO :: 1.90430 : 0.47036$$

whence, as before,

$$12y + 162.144 : 4x :: 1.43394 : 0.47036$$

or

$$(b)\quad 0.35848x - 0.35277y = 4.7666282$$

combining a and b and eliminating

$$x = 25.112$$

$$y = 12.007$$

whence the atomic weight of beryllium is 9.112 and that of carbon is 12.007 as compared with 9.113 for beryllium as previously reported.

The rigorous rule in such a calculation would be to give each equation weight inversely proportional to the square of its probable error, but as in my first calculations the figures obtained for the atomic weight of beryllium from both the acetylacetonate and the basic acetate were identical, an application of this rule would have little influence upon the result.

The close agreement of the figures obtained by this method of calculation with the accepted weights is especially noteworthy

[1] *Ann. Chem.* (Liebig), **59**, 280.
[2] *Am. Chem. J.*, **13**, 34.
[3] *Ibid.*, **27**, 321.
[4] This Journal, **26**, 737.
[5] *Ibid.*, **26**, 740.

when the fact is taken into consideration that a very small variation in the amount of beryllium oxide in either of the above equations would largely affect the result for carbon.

The conclusion seems warranted that the atomic weight of beryllium is very close to 9.112, or that there is an equal and balancing error in both equations.

NEW HAMPSHIRE COLLEGE,
June 15, 1905.

CHARLES LATHROP PARSONS.

Changes of Color Caused by the Action of Certain Rays on Glass.—In the Journal, Vol. 27, page 909, under the above title, appeared certain comments by S. Avery relative to glass becoming violet on exposure to the sun's rays. As there pointed out, the color appears to be dependent upon the presence of manganese originally in the glass, and the intensity of the color is approximately proportional to the manganese present. The occurrences reported by Mr. Avery and Sir Wm. Crookes resulted from exposures to the sun's rays in New Mexico and South America. Among the quotations from Sir Crookes, is: "It would be interesting to hear if travelers in other tropical countries have observed any such change of color of glass." Apparently, the inference is that there is a connection between the phenomenon and the sun's rays in the tropics.

My attention was recently attracted by a similar occurrence in the Butte District, in Montana, U. S. A. The northern part of this district contains large ore bodies, in which manganese as dioxide is a very prominent component. Seemingly, all colorless glass which is allowed to remain for some years on this surface, exposed to the sun's rays, shows a violet color of greater or less intensity. This color is not merely a superficial coating, but extends completely through the glass. The writer never investigated the cause, but is personally able to vouch for the fact of actual occurrence. The color would naturally suggest the presence of manganese, either originally in the glass or derived from extrinsic sources. On account of the proximity of bodies heavily charged with manganese, the latter inference was a possible one, although I considered it hardly probable in view of the fact that most colorless glass contains manganese. It is, however, evident that the phenomenon is not confined to the tropics.

CHAS. E. RUEGER.

NEW BOOKS.

MANUAL OF CHEMICAL ANALYSIS AS APPLIED TO THE ASSAY OF FUELS, ORES, METALS, ALLOYS, SALTS AND OTHER MINERAL PRODUCTS. By EUGENE PROST, D.Sc., of the University of Liège. Translated from the original by J. CRUIKSHANK SMITH, B.Sc., F.C.S., some time Chief Assistant Department of Technological Chemistry, Glasgow, and West of Scotland Technical College. London, Eng.: Maclaren and Sons. New York: D. Van Nostrand Co. 1904. vii + 300 pp. Cloth. Price, $4.50 net.

The author has brought together in this hand-book a collection of methods for the analysis of the chief mineral products, both native and manufactured, with which the industrial or metallurgical chemist has to deal. These methods have been selected from those which have commended themselves to the author, or have been communicated to him by "specialists of large experience."

The subject-matter is divided into three parts, of which Part I includes the analysis of fuels, of water for hardness only, and of the important compounds of each of the common metals, arranged in chapters under each metal. Part II deals with the analysis of irons and steels, and of copper, zinc, lead, aluminum, tin, nickel, and antimony, while Part III describes the analyses of such alloys as the brasses, bronzes, aluminum alloys, antifriction metals, fusible metals, and alloys of silver and gold.

The analytical procedures are preceded by a brief description of the important properties of the commercial product under discussion, and, frequently, by typical results of analysis.

Every author who places before his co-workers a collection of analytical procedures which he is willing to guarantee to be reliable is worthy of full recognition for the boon conferred, provided, of course, that he speaks from a full experience. In the present instance the methods presented appear to be mostly those of recognized usefulness, and these methods are described in considerable detail. It is natural that the selection of processes should reflect the usage of the continental laboratories abroad, and this brings the book, as a whole, somewhat out of accord with American analytical practice. While it does not appear to contribute much material for which freshness or originality can be claimed, it is, nevertheless, to be respected in its purpose, as outlined above, and both practising analysts and students will find it worthy of attention.

The translator has done his part commendably, the proof-readers somewhat less so, as errors and crooked lines are not by any means lacking (notably on page 75, and in equations on pages 57, 108, 121, and 130). The peculiar quality of paper chosen appears to be responsible for indistinctness in many small letters and figures. H. P. TALBOT.

PHARMACOLOGY OF THE FLUID EXTRACTS IN COMMON USE. BY JOHN S. WRIGHT. Indianapolis: Eli Lilly and Co. 1905. 225 pp. Price, 50 cents.

It is a valuable little handbook containing much information in a very concise form, useful alike to the busy practitioner of medicine and to the dispensing pharmacist. Being brief, it does not go into minute details or into a discussion of doubtful points. The list of common and botanical synonyms and general index make it easily possible to ascertain the pharmacological action of any drug described in the book. In order to make it more valuable and complete, a few drugs not exhibited in the form of fluid extracts, are included. The last pages are devoted to poisons and antidotes, weights and measures, and a very complete list of abbreviations used in prescription writing. It is printed upon good paper and bound in flexible leather. W. H. BLOME.